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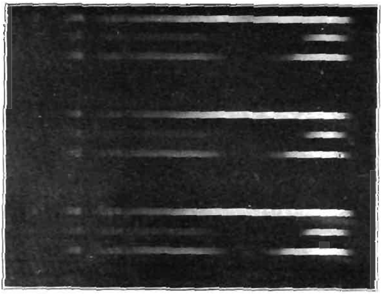

PLATE I.

Air and vacuum.
Excess of I_2.

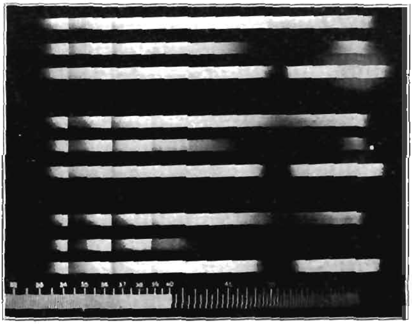

PLATE II.

Argon and vacuum.
Excess of I_2

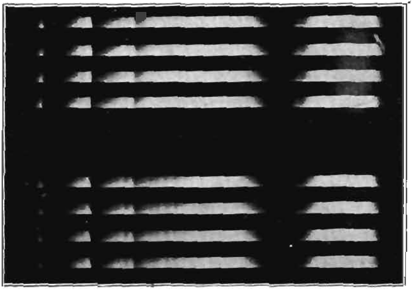

PLATE III.

Spectra of I_2 vapour in air, nitrogen, oxygen and CO_2.

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List of Physico-chemical Symbols adopted by the Chemical Society.
[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c; t_c, T_c; d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r; t_r, T_r, d	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	$K, (K_c, K_p)$	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

	Usual symbol.	Alternative symbol.
Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]^{t°}_{\lambda}$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]^{t°}_{\lambda}$	
Molecular refractive power	R_G, R_L $[R_G]^{t°}_{\lambda}$, $[R_L]^{t°}_{\lambda}$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

	Usual symbol.	Alternative symbol.
Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ_c
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon_c$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_{∞}	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions...	$\Lambda_K \cdot \Lambda_{Cl}$	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion ...	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; *molecular heat.*
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
d	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_eE_h, {}_eE_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	*Critical pressure : reduced pressure.*
Q	Quantity of heat; quantity of electricity.
R	*Gas constant per mole; electrical resistance.*
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	*Critical volume : reduced volume.*
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h$, ${}_0\epsilon_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, *when the solution is molecular-normal* in respect of all participating substances and ions of variable *concentration* (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
Λ_{32}, Λ_v, Λ_∞	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

. —*The Thermal Decomposition of Ammonia, with Particular Reference to the Existence of Active and Inactive Phases of Ammonia.*

By William Arthur Stringfellow.

'he work now described was undertaken in order to test the con- lusion of Baly and Duncan (J., 1922, **121**, 1008) that ammonia as formed by very rapid evaporation of the liquid is decomposed ›ss rapidly by a hot platinum wire than that obtained by slow vaporation, but their results could not be confirmed.

The method used was based upon that of Baly and Duncan, so ır as the information given in their paper allowed.

Sources of Ammonia.—Two cylinders of liquid ammonia were sed, one of synthetic ammonia, which was connected directly to he apparatus, and the other of gas-works origin, from which liquid 'as drawn off into a vessel, suitably protected from the atmosphere, hich could then be attached to the apparatus.

Variation of Rate of Evaporation.—Ammonia gas from the cylinder r other source was condensed, after passing very slowly through wo drying tubes, each 70 cm. long and containing quicklime, or hrough an alternative direct connexion, in one or other of the hree vessels, A, B, or C (Fig. 1). Vessel A was used for slow othermal evaporation; the actual rate of gas formation therefrom 'as about 15 c.c. per minute. From B the liquid could be evapor- ted very quickly, by allowing it to be forced up the capillary to ıe bulb D by the pressure of its own vapour. Vessel C could be sed for rapid boiling by direct heating. From either B or C vaporation readily occurred at the rate of 10,000 c.c. of gas per ıinute, and this rate was often exceeded. These alternative ıethods of rapid evaporation gave identical results in the decom- osition experiments.

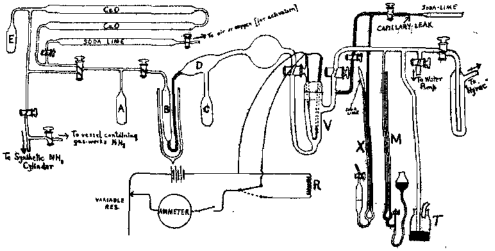
Reaction Vessel.—This vessel, V, which was kept in a thermostat ıaintained at 20°, was provided with inlet and outlet tubes of mm. bore, to cope with the rapid flow of gas. The platinum wire, bout 9 cm. long and of 40 gauge, was welded to stout platinum

wires sealed into tubes passing through a "slip-joint" top to the vessel, so that the wire could be easily removed and replaced. The reaction vessel was connected by a ½-mm. capillary tube over 1 m. long to a manometer, X, containing xylene, which was chosen because it had been used by Baly and Duncan.

Temperature Control.—The wire was heated by means of a battery of accumulators. The time during which current passed was recorded on a 1/5-second stop-watch, arranged so that the actual "make" and "break" movements started and stopped it.

Current was measured on an open-scale Weston ammeter reading direct to 0·02 amp. and allowing easy estimation to 0·002 amp. Measurements of *E.M.F.* also were made in preliminary work, but

FIG. 1.



were discontinued, since actual measurements of the wire temperature were not desired. Reproducibility of temperature was secured by the use of an auxiliary resistance, R, kept at constant temperature in the thermostat, and roughly equal to the resistance of the reaction wire, which could be made to form an alternative path for the current by means of the three-way switch. This alternative resistance was used suitably to adjust the value of the current before making connexion *via* the reaction wire, and again to check it after breaking this connexion. If, in successive experiments, a given current through R corresponds to identical values of current through the reaction wire, then, since the *P.D.* across the latter is the same in each case, its resistance and hence the energy input must be the same in each experiment. This disposes of the possibility that the same current might cause different heating effects due to variation of the resistance.

Owing to the extra cooling effect caused by the hydrogen formed, the resistance of the platinum wire must alter slightly during the

course of an experiment. The "drift" in the current due to this was found to be very small—of the order of 0·002 amp.—during the 20-second periods used. No attempt was made, therefore, to keep the current constant by continuous adjustment of resistance, but in order to ensure more comparable results, its value was always read 5 seconds after the reaction started.

Filling of Reaction Vessel.—The vessel was exhausted fairly thoroughly by a "Hyvac" pump, after the bulk of any ammonia present had first been removed by a water-pump. Sufficient ammonia was then allowed to evaporate through it to fill it about five times over, the excess escaping *via* a mercury trap, T.

Care was usually taken that only a part of the liquid in the evaporation vessel was used, about one-third being left behind; for, if the effect observed by Baly and Duncan were due to partial separation of the constituents of an impure ammonia, the effect might be annulled if the residuary portion evaporated. In certain instances, indicated in the table below, this precaution was not observed. The gas filling the reaction vessel was, prior to decomposition, brought to exactly 760 mm. pressure by means of a capillary leak, L, and manometer adjustment, M. The reaction vessel was in every case heated for a period of 20 seconds, as in Baly and Duncan's experiments. After thermal equilibrium had been restored, connexion was made to the xylene manometer and the increase in pressure at constant volume recorded.

Preliminary Experiments.—In a series of decompositions carried out with gas direct from the cylinder, without intermediate condensation, somewhat discordant results were obtained. The decomposition rate was found to vary considerably, depending upon the history of the platinum wire between successive experiments, *e.g.*, on the time during which vacuum was maintained, and on intervals elapsing between operations. By adopting a uniform practice in these details the difficulty was largely overcome, but variations were always liable to occur after any interruption, and results could only be taken as truly comparable when the "rapid" and "slow" methods were used alternately, in quick succession.

"Rapid" and "slow" experiments with the unactivated wire, in which the ammonia used was (1) synthetic, (2) gas-works, (3) quicklime-dried, and (4) undried, gave substantially identical results for the rate of decomposition.

Activation of the Wire.—Attempts were then made to activate the wire by the methods described by Baly and Duncan.

The first method, in which the wire was alternately heated and cooled to about 500° for some hours, failed to produce the results claimed. Baly and Duncan do not refer to any actual measurements

of wire temperature, but in the present work temperatures were roughly estimated by the brightness of glow, and, both in activation and decomposition experiments, a range of temperatures was employed (*e.g.*, 600—1100° for decomposition) which must certainly have included such values as were used by those authors. This first activation process was carried out both in air, at atmospheric pressure, and in a vacuum (Baly and Duncan do not state the medium).

The second method, that of heating the wire to bright redness in a stream of air and ammonia until its temperature begins to rise and it continues to glow when the current is switched off, was also tried. In carrying out this process, difficulties arose from the fact that traces of ammonium nitrate, formed during the initial stages of the ammonia oxidation, condensed on the walls of the vessel. This caused a negative pressure drift after admission of ammonia for the decomposition experiments, owing to the solubility of ammonia in the nitrate, and a positive drift after the decomposition, due to the release of ammonia from the solution when its partial pressure in the gas phase was reduced. This could be allowed for to some extent, but the most satisfactory, though time-consuming method was to remove the wire after activation and clean the vessel, taking care not to expose the wire to treatment likely to impair its activity, and then to replace it. That this cleaning did not affect the activity was shown by the fact that, after it had been carried out, the wire was capable of showing the "after-glow" effect on being heated for a few seconds in an air–ammonia mixture.

So far, no success has attended repeated attempts to activate a wire so that it behaves differently towards the rapidly and the slowly formed gas. Several wires have been tried, the temperatures during activation have been varied, various proportions of air and ammonia have been used, and ammonia–oxygen mixtures have also been employed. The time of activation by this second method has been prolonged up to 3½ hours after the first appearance of the after-glow.

Experiments have been made in which the ammonia has been distilled backwards and forwards slowly up to eight times through the lime tubes (between bulb A and bulb E), in case it might otherwise retain sufficient moisture to annul the effect under investigation, for, according to Baly and Duncan, water vapour can render inactive ammonia active. No difference in decomposition rate resulted.

The wire used was of ordinary commercial platinum; and since this showed the usual signs of being susceptible to such activation as rendered it suitable for ammonia oxidation, it does not appear likely that it contained any impurity that would unfit it for demonstrating the effect noted by Baly and Duncan.

Results.

Data obtained with five different wires are given below. The first column of each table contains observed values (C) of the current in amps.; cols. 2 and 3 show the pressure increases (in cm. of xylene) P_S and P_R for slow and rapid evaporation, respectively; cols. 4 and 5 give the corresponding calculated percentage decompositions, x_S and x_R (corrected, see below); and in the last column is given E, the percentage difference (to the nearest 0·1 unit) between the values of x_S and x_R, this difference being reckoned positive when the decomposition value is greater for slowly evaporated ammonia, *i.e.*, when it is such as to tend to confirm Baly and Duncan's observation.

Since it was impossible always to get a pair of identical values for C for the corresponding slow and rapid experiments, in all cases where these differed the values of x_R given in col. 5 have been calculated so as to correspond to a current value equal to that in the slow evaporation. The necessary corrections were obtained graphically from the values of dx/dC at various values of C. Whenever the observed values of the current in corresponding "slow" and "rapid" experiments differed by more than 0·002 amp., the observations were rejected. In 41 out of the 86 observations herein recorded, the C_{rapid} and C_{slow} values were actually identical, and the correction necessary in the other cases was in only one case greater than 2% of the value of x_R.

(*a*) Wire No. 1, activated by alternate heating and cooling to about 500° for 4 hours.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·872	16·44	16·03	2·16	2·13	+1·5
1·896	18·14	18·78	2·39	2·47	−3·3
1·942	22·69	22·61	2·99	2·94	+1·6
1·984	29·38	29·14	3·87	3·75	+3·1
1·990	30·96	31·33	4·07	4·06	+0·2
		(2)			
1·882	17·00	17·09	2·24	2·26	−0·9
1·952	23·76	23·60	3·13	3·10	+1·0
1·968	26·65	26·50	3·51	3·47	+1·1
1·992	32·26	32·99	4·24	4·34	−2·4
		(3)			
1·870	16·02	16·21	2·11	2·13	−1·0
1·922	20·40	20·08	2·68	2·62	+2·3
1·972	26·55	26·86	3·49	3·56	−2·0
1·994	31·34	31·49	4·12	4·14	−0·5
		(4)			
1·858	15·12	15·01	1·99	2·00	−0·5
1·894	18·10	18·66	2·38	2·44	−2·5
1·932	21·36	21·11	2·81	2·78	+0·7
1·972	27·68	27·39	3·64	3·62	+0·6
1·996	35·74	35·66	4·70	4·69	+0·2

(*b*) Wire No. 2, after 2 hours' activation by "ammonia oxidation" method.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·874	15·06	15·82	1·98	2·06	−4·0
1·894	16·47	16·30	2·17	2·16	+0·5
1·954	22·31	22·79	2·94	3·00	−2·0
1·998	32·60	33·48	4·30	4·28	+0·5
		(2)			
1·916	18·34	18·22	2·41	2·39	+0·8
1·954	22·67	22·00	2·98	2·92	+2·0
1·998	32·07	31·95	4·22	4·30	−1·9
		(3)			
1·888	15·92	15·64	2·09	2·06	+0·5
1·944	20·97	20·82	2·76	2·75	+0·4
1·998	32·51	33·34	4·28	4·27	+0·2
		(4)			
1·036	20·35	20·87	2·68	2·72	−1·5
1·954	22·68	22·36	2·98	2·94	+1·3
1·972	24·95	24·57	3·28	3·28	±0·0
1·988	27·50	27·61	3·62	3·70	−2·2
2·006	35·99	35·79	4·73	4·71	+0·4

(*c*) Wire No. 3, activated by heating and cooling, followed by 2 hours' ammonia-oxidation treatment.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·936*	20·92	20·60	2·75	2·74	+0·4
1·940*	21·44	21·65	2·82	2·85	−1·0
1·946	22·73	22·50	2·99	2·92	+2·3
1·984	29·09	28·67	3·83	3·73	+2·6
1·988	30·10	30·24	3·96	4·03	−1·7
1·994*	31·78	31·42	4·18	4·13	+1·2
		(2)			
1·938	21·02	20·77	2·76	2·73	+1·2
1·942	21·74	21·89	2·86	2·88	−0·7
1·982	27·85	28·19	3·66	3·75	−2·4
1·996	32·16	31·66	4·23	4·22	+0·2
		(3)			
1·894*	17·24	17·20	2·27	2·23	+1·7
1·920*	19·95	19·57	2·63	2·64	−0·4
1·954*	23·56	23·50	3·10	3·09	+0·3
1·970	25·75	25·98	3·39	3·39	±0·0
1·984	28·74	29·31	3·78	3·86	−2·1
		(4)			
1·890	17·27	17·14	2·27	2·29	−0·9
1·916	19·29	19·48	2·54	2·60	−2·2
1·950	23·80	23·04	3·13	3·07	+2·3
1·974	26·42	26·31	3·48	3·46	+0·6
1·984	29·86	30·24	3·93	3·98	−1·2

(*d*) Wire No. 4, activated by oxidation method for about 2 hours in air–ammonia mixture, and later for 1 hour in oxygen–ammonia mixture.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·870	16·08	16·27	2·12	2·14	−0·9
1·948	23·46	24·01	3·09	3·16	−2·3
2·066	37·38	37·12	4·92	4·88	+0·8
		(2)			
1·860	15·51	15·78	2·04	2·05	−0·5
1·904	19·32	19·39	2·54	2·55	−0·4
1·986	30·34	30·30	3·99	4·01	−1·7
1·986	30·42	30·06	4·00	3·95	+1·2
		(3)			
1·880*	17·24	16·69	2·27	2·22	+2·2
1·894*	18·32	18·39	2·41	2·44	−1·3
1·936	22·20	22·68	2·92	2·96	−2·0
1·966	25·24	25·03	3·32	3·33	−0·3
		(4)			
1·862	16·92	16·20	2·23	2·15	+3·6
1·910	20·02	20·52	2·63	2·69	−2·2
1·972	27·20	27·38	3·58	3·55	+0·8
1·990	34·25	34·16	4·51	4·49	+0·4
2·002	36·36	36·60	4·78	4·80	−0·4

(*e*) Wire No. 5, activated for 3½ hours by oxidation method.

C.	P_S.	P_R.	x_S.	x_R.	E.
		(1)			
1·922	14·77	15·14	1·94	1·99	−2·6
1·956*	15·26	15·31	2·01	2·01	±0·0
1·988	15·74	15·95	2·07	2·10	−1·4
2·046*	17·20	17·33	2·26	2·27	−0·5
2·070	17·64	17·49	2·32	2·30	+1·3
		(2)			
1·926	14·92	14·81	1·96	1·95	+0·5
1·944†	15·10	15·42	1·99	2·03	−2·0
1·970†	15·53	15·48	2·04	2·04	±0·0
2·024	16·57	16·79	2·18	2·20	−1·4
2·056	17·16	17·02	2·26	2·24	+0·9
2·148	20·53	20·13	2·70	2·66	+1·5
		(3)			
1·950	15·22	15·24	2·00	2·00	±0·0
1·984*	15·73	15·40	2·07	2·03	+1·9
2·058*	17·28	17·45	2·27	2·28	−0·5
2·094	18·11	18·30	2·38	2·42	−1·7
2·134*	19·65	19·32	2·59	2·54	+1·9
		(4)			
1·934†	14·90	15·23	1·96	2·00	−2·0
1·990†	15·96	15·74	2·10	2·08	+0·9
2·032	16·80	16·85	2·21	2·21	−0·4
2·088	17·81	18·04	2·34	2·37	−1·3
2·110†	18·64	18·90	2·45	2·48	−2·8
2·168	21·58	21·30	2·84	2·80	+1·4

* In these experiments the contents of the evaporation vessel were allowed to evaporate completely.

† In experiments marked thus, the ammonia was distilled several times through the drying tubes (see p. 4).

In the tables, the experiments are classified according as the ammonia was (1) synthetic, direct from cylinder; (2) synthetic, dried by passing once over lime (except those marked †); (3) gas-works, direct from cylinder; (4) gas-works, dried as in (2).

Summary of Results.

Kind of ammonia used.	Total no. of expts.	No. of expts. giving *positive* effect, and average value of effect.	No. of expts. giving *negative* effect, and average value of effect.
Synthetic (undried)	22	12, +1·3%	10, −1·0%
Synthetic (dried)	20	10, +1·0%	10, −1·4%
Gas-works (undried)	19	9, +1·3%	10, −1·2%
Gas-works (dried)	25	12, +1·1%	13, −1·5%

Discussion and Conclusions.

According to Baly and Duncan, rapidly evaporated ammonia showed a decrease in reactivity, compared with slowly evaporated, of from 25% to 50%, the higher value being obtained for low temperatures of the reaction wire. The above data do not in any way confirm their results: if anything, they establish a very small negative effect, but this may be ascribed to some systematic error in the method. In the present work, the "rapid" experiments were in nearly every case made directly after the "slow," whilst short intervals separated the latter from the succeeding "rapid" ones.

Baly and Duncan state that "the addition of water vapour *very greatly* increases the amount of decomposition by a definite amount of energy." The present results do not confirm this observation. It should be pointed out, however, that Baly and Duncan do not specify the degree of wetness or dryness necessary to establish this difference, and the variation in moisture content may have been greater in their samples. They attribute the effect which they observed to the existence of two molecular species in equilibrium in liquid ammonia, one of less energy content than the other, and they consider that, whereas in slow evaporation all molecules assume the more active form on evaporation, in the case of rapid ebullition the balance between active and inactive phases to some extent persists in the gaseous state.

The maintenance of this kind of metastable equilibrium in a gas phase seems somewhat doubtful. The fact that a heterogeneous decomposition was involved in testing the "reactivity" of the gas suggests at once that the effect was due to some variation of the catalyst surface. Briscoe (*Ann. Report*, 1922, **19**, 37) points out that ammonia dried over quicklime may retain a relatively large amount of moisture, and in view of Mulliken's statement (*J. Amer. Chem. Soc.*, 1922, **44**, 2389), that rapid irreversible distillation may effect partial separation even of the constituents of a constant-boiling mixture, he suggests that the ammonia gas formed by very rapid evaporation may have been appreciably the drier. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 268) favours this

explanation, but the negative results of the present investigatio do not support it.

Baly and Duncan refer to a streaming method of filling thei vessel, and do not mention prior exhaustion of the latter. If ai or products of a previous decomposition, were present before th ammonia was admitted, it appears possible that, owing to eddies se up, very rapid streaming might result in their not being so com pletely displaced as by the slow passage of the same quantity o ammonia, and that the presence of adsorbed residuary gases on th wire might inhibit the reaction. It is noteworthy that Baly an Duncan found the greatest effect for low wire temperatures, a which adsorbed gas would be more firmly held.

It is concluded from the results of the present investigation tha the effect observed by Baly and Duncan was dependent upo factors not explicitly defined in their paper, and did not resu from the existence of different phases of gaseous ammonia.

The author wishes to express his thanks to Professor F. G. Donnan F.R.S., for suggesting this research and for his kind advice an criticism.

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, November 2nd,* 1928.]

II.—*Influence of Poles and Polar Linkings on Tauto merism in the Simple Three-carbon System. Part I Experiments illustrating Prototropy and Anionotrop in Trialkylpropenylammonium Derivatives.*

By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN.

ONE of the most immediate consequences of the acceptance of th electronic theory of valency is that the double-bond displacemer involved in the various phenomena grouped under the name tau tomerism is to be interpreted as an electron-duplet displacemer entailing a redistribution of electrical charges (the "tautomer electron-displacement," *T*). The study of tautomerism—both cationotropy and anionotropy—is, on this view, a study of th conditions affecting charge-distribution by the *T*-displacement and, since some of the major reactions of Organic Chemistry, as, fo example, additions to conjugated unsaturated systems, and sub stitutions in aromatic systems, are believed to depend largely o this type of charge-transference between *carbon* atoms, fundament

information is to be gained by an examination of prototropic and anionotropic transformations in the *true three-carbon* system.

The large accumulation of data, for which we are indebted mainly to Kon and Linstead, regarding "three-carbon" prototropy relates exclusively to systems terminated by unsaturated groups such as carbonyl: C[H]·C:C·C:O ⇌ C:C·C:C·O[H] ⇌ C:C·C[H]·C:O. The systems are, indeed, pentad (*e.g.*, pentad keto-enol); but in so far as the enolic intermediate can be neglected there is some justification for regarding them as the equivalent of three-carbon systems: the relation between the ketonic forms at equilibrium will depend *inter alia* on anionic charge-distribution in the C·C:C-group (Ingold, Shoppee, and Thorpe, J, 1926, 1477). Prototropy in the *elementary* three-carbon system, that is, the C·C:C-group joined to saturated radicals only, has not yet been studied, and we have therefore undertaken to repair this omission.

Amongst the saturated groups which suggest themselves as likely to fulfil the primary necessity of loosening the potentially mobile proton by the attraction of its electrons are $-NR_3{}^{\cdot}$, $-SR_2{}^{\cdot}$, $-SO_2R$, $-SO_3{}'$, and the work here to be described utilises the first of these. Since unsaturated diammonium bases of the type

$$\overset{\ominus}{O}H\{R_3\overset{\oplus}{N}\cdot CH_2\cdot CH{:}CH\cdot\overset{\oplus}{N}R_3\}\overset{\ominus}{O}H$$

(like glutaconic acid, except that $\cdot NR_3$ replaces $\cdot CO_2H$) have not yet been prepared, some exploratory work was necessary, and it was during the examination of a possible route to such compounds that we unexpectedly encountered evidence, not only of prototropic, but also of anionotropic, mobility * in three-carbon systems terminated by one ammonium-salt group only.

Starting from γ-chloroallyl chloride, no difficulty was experienced (see scheme below) in obtaining quaternary γ-chloroallylammonium salts of the type $\{CHCl{:}CH\cdot CH_2\cdot N(alk)_3\}^{\cdot}X'$, but the chlorovinyl chlorine atom in these could not be induced to enter into reaction with secondary or tertiary amines. This had been anticipated, and our plan was to subject the cations of these salts to the attack of an anion of high co-ordinating power; the electron-affinity of $-\overset{\oplus}{N}R_3$ might then, we supposed, induce the liberation of an α-proton with the subsequent formation of the isomeric salts

$$\{CH_2Cl\cdot CH{:}CH\cdot N(alk)_3\}^{\cdot}X',$$

which, since they are allyl chlorides, should readily react with tertiary amines to give the required diammonium compounds. The effect of treating the γ-chloroallyl salts with sodium ethoxide in warm alcohol was to produce a series of ethoxy-salts, which were at first thought to

* Prototropic mobility in such salts was predicted by one of us in 1926 at the meeting of the British Association in Oxford.

have the constitution $\{CH_2(OEt)\cdot CH{:}CH\cdot N(alk)_3\}^{\cdot}X'$; but their properties (especially the difficulty attending the replacement of OEt by Br) aroused suspicion. Investigation then showed that these salts possessed the constitution $\{CH_2{:}CH\cdot CH(OEt)\cdot N(alk)_3\}^{\cdot}X'$, ozonolysis yielding, in each case, formaldehyde and an ethoxyaldehydoammonium salt of the general formula $\{CHO\cdot CH(OEt)\cdot N(alk)_3\}^{\cdot}X'$.

In retrospect it is obvious that such a result might have been anticipated. The potentially mobile atom being shown in square brackets, the salts, $\{CHCl{:}CH\cdot CH[H]\cdot N(alk)_3\}^{\cdot}X'$, contain a prototropic system only, but their tautomerides,

$$\{CH[H]Cl\cdot CH{:}CH\cdot N(alk)_3\}^{\cdot}X' = \{CH_2[Cl]\cdot CH{:}CH\cdot N(alk)_3\}^{\cdot}X',$$

have in addition an anionotropic system, which, since its mobile atom is a halogen, would be expected to function under the conditions which were established in order to effect the primary prototropic change (Burton and Ingold, J., 1928, 904). Furthermore the proved *connexion* (*loc. cit.*) between the *facilitation of* an ionotropy by groups and their orienting action in aromatic substitution, when applied to the anionotropic system $H\text{—}\overset{\frown}{CH\cdot CH{:}CH}\text{—}\overset{\oplus}{N}R$ (anion omitted), requires that the order of facilitation shall be $H > \overset{\oplus}{N}R_3$; wherefore analogy suggests that the position of stable attachment of the mobile anion should be that adjacent to the ammonium group. But further, the production of an *isomeride* from a mobile anionotropic system depends on the absence from the medium of foreign anions having a greater co-ordinating power than that possessed by the anion derived from the system itself (Burton, J., 1928, 1650). This condition is not fulfilled in the present instance, and it is evident that the chloride ion originally eliminated would have small chance of returning to the system in the face of competition from the large concentration of ethoxide ions present in the medium. Thus, after the reaction, free chloride ions are present, ethoxide ions have disappeared, and the original chloro-salt has given place to an ethoxy-salt of the constitution $\{CH_2{:}CH\cdot CH(OEt)\cdot N(alk)_3\}^{\cdot}X'$.

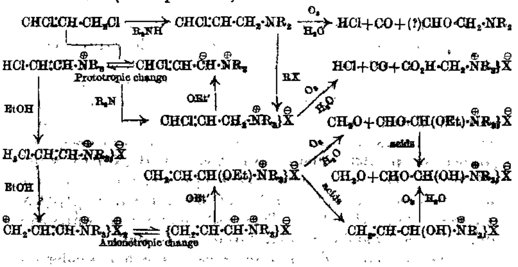
Furthermore, our failure to effect replacement of the OEt-group in these salts by Br, by methods normally successful with allyl ethers, is readily understood, for the same electron-affinity of the $N(alk)_3$-group which determines the stable attachment of ethoxyl must also cause its shared electrons to be exceptionally deeply implicated in the constitution of the α-carbon atom, and must accordingly inhibit any reaction involving the separation of ethoxyl *with these electrons*. If this is correct, then, for an exactly similar reason, the ammonium group should facilitate the separation of ethyl *without* its shared electrons; in other words, the ethoxy-

compounds should in certain respects resemble esters rather than ethers. Of course there are limits to the analogy represented by

$$R\to O\to \overset{|}{\underset{|}{C}}\to \overset{\oplus}{N}(alk)_3 \quad \text{and} \quad R\to O\to \overset{|}{\underset{|}{C}}=O.$$

For instance, it would not apply to *alkaline* saponification, which, in the case of carboxylic esters, depends (addition of OH′ at carbonyl) on an unsaturated linking absent from the ammonium salts. But as regards *acid* hydrolysis, in which the seat of attack (by hydrogen ions) is the unshared electrons of the singly-bound oxygen atom, the two systems should show their similarity. Experiment showed that the ethoxy-salts are in fact as readily hydrolysed by acids as are many carboxylic esters, and we confirmed our view that the presence of the vinyl group has nothing to do with the matter by showing that the ethoxyaldehydo-salts, obtained by ozonolysis, could be hydrolysed in the same way with similar facility.

Other transformations, which need no special comment, as, for instance, ozonolysis of the chloro- and hydroxy-salts to products establishing their constitutions, are included in the scheme given below, in which R represents methyl or ethyl, and X a univalent anion (chloride, acetate, picrate, etc.) or a semi-equivalent of a bivalent anion (chloroplatinate):



EXPERIMENTAL.

Diethyl-γ-chloroallylamine and its Salts.—γ-Chloroallyl chloride (10 g.) was mixed with diethylamine (14 g.) under an efficient reflux condenser. When the vigorous reaction had ceased, the product was mixed with aqueous sodium hydroxide and extracted with ether; thereafter diethyl-γ-chloroallylamine was obtained as a colourless liquid, b. p. 55°/9 mm. (yield, 75%). The hydrochloride was very soluble in water, but separated from acetone in plates, m. p. 221°. The *picrate* crystallised from water in prismatic needles,

m. p. 78° (Found: C, 41·7; H, 4·7. $C_{13}H_{17}O_7N_4Cl$ requires C, 41·4 H, 4·5%).

Triethyl-γ-chloroallylammonium Salts.—(*a*) The tertiary base (7 g. was warmed with ethyl iodide (15 g.) in ethyl alcohol (10 c.c.) unde reflux, and the quaternary iodide precipitated as a pale yellow crystalline solid by addition of much ether. It was dissolved i alcohol, reprecipitated by the addition of ether, and crystallise from acetone, from which it separated in needles, m. p. 210°. Treat ment with aqueous sodium picrate gave a *picrate*, which crystallise from water in narrow prisms, m. p. 125° (Found: C, 43·8; H, 5·3 $C_{15}H_{21}O_7N_4Cl$ requires C, 44·5; H, 5·1%).

(*b*) A mixture of γ-chloroallyl chloride (15 g.), triethylamine (15 g. and ethyl alcohol (15 c.c.) was heated under reflux for 20 minute with precautions against entrance of moisture. After 14 hour ether (600 c.c.) was added and the hygroscopic chloride collected This on treatment with sodium picrate gave the above picrat Interconversion of the chloride and iodide has been effected throug the hydroxide obtained from either with silver oxide and water.

The complete series of transformations, including ozonolysis described below, the starting point of which was a triethyl-γ chloroallylammonium salt, has been carried out in duplicate wit material prepared by the methods (*a*) and (*b*). These salts could no be induced to react with triethylamine at temperatures up to 100°

Trimethyl-γ-chloroallylammonium Salts.—γ-Chloroallyl chlorid (20 g.) was added with cooling, under reflux, to alcoholic trimethy amine (68 c.c. of 33% solution). After the completion of the reactio the deliquescent *chloride* was precipitated with ether (600 c.c.), an crystallised from acetone, from which crystals separated, m. p. 63° which on drying in a vacuum effloresced, leaving a microcrystallin powder, m. p. 193° (Found: Cl′, 20·5. $\{C_6H_{13}NCl\}^{\bullet}Cl'$ require Cl′, 20·9%). The corresponding *picrate* separated from water or dilut alcohol in needles, m. p. 141° (Found: C, 39·9; H, 4·4. $C_{12}H_{15}O_7N_4Cl$ requires C, 39·7; H, 4·2%). These salts did not react with diethyl amine or triethylamine at temperatures up to 100°.

Triethyl-α-ethoxyallylammonium Salts.—Triethyl-γ-chloroallyl ammonium chloride (or iodide) was warmed with an alcoholi solution of sodium ethoxide (2 mols.) prepared from sodium (5·5 g. and ethyl alcohol (90 g.). When no further quantity of sodium chloride separated (or after an equal time in the case in which th iodide was used), the solution was filtered and evaporated belov 60°. The residual ethoxide was converted into the *picrate* by th addition of alcoholic picric acid. The salt separated from ethy alcohol in narrow prisms, m. p. 122—123° (Found: C, 48·9; H, 6·2; OEt, 11·3. $C_{17}H_{26}O_8N_4$ requires C, 49·3; H, 6·3; OEt, 10·9%).

Trimethyl-α-ethoxyallylammonium Salts.—The ethoxide was prepared in a similar way from trimethyl-γ-chloroallylammonium chloride, and converted into the *picrate*, which separated from ethyl alcohol in narrow prisms, m. p. 111—112° (Found: C, 45·2; H, 5·6; OEt, 12·2. $C_{14}H_{20}O_8N_4$ requires C, 45·2; H, 5·4; OEt, 12·1%).

Triethyl-α-hydroxyallylammonium Salts.—Triethyl-α-ethoxyallylammonium chloride, prepared from the ethoxide, was warmed for a short time with concentrated hydrochloric acid, and the excess of acid evaporated. The residual chloride was a viscous syrup which could not be crystallised, but the addition of aqueous sodium picrate yielded a picrate, which crystallised from water in prismatic needles, m. p. 145°, and chloroplatinic acid gave a *chloroplatinate*, which separated from water in orange needles (Found: C, 29·7; H, 5·5. $C_{18}H_{40}O_2N_2Cl_6Pt$ requires C, 29·8; H, 5·5%).

Trimethyl-α-hydroxyallylammonium Salts.—The chloride was obtained as an uncrystallisable syrup from trimethyl-α-ethoxyallylammonium chloride, as in the last experiment. The *picrate* separated from dilute alcohol in prisms, m. p. 149° (Found: C, 42·1; H, 5·0. $C_{12}H_{16}O_8N_4$ requires C, 41·9; H, 4·7%).

Fission by Ozone of Diethyl-γ-chloroallylamine: Formation of Hydrogen Chloride, Carbon Monoxide, and a Base.—A solution of the amine in ligroin was treated with ozonised oxygen for 24 hours. A deep red, liquid ozonide separated from solution as a lower layer. It was boiled with water, in which it dissolved; carbon monoxide was evolved (gas, insoluble in a solution of *p*-nitrophenylhydrazine acetate, giving blue flame on ignition in air), and chloride ions appeared in the solution, which was acid to litmus. The non-precipitation of a *p*-nitrophenylhydrazone indicated the absence of formaldehyde. The concentrated residual solution gave a chloroplatinate, which owing to its instability was difficult to purify, but which from its properties and composition in the crude state may have been the chloroplatinate of diethylaminoacetaldehyde, although we cannot assert this definitely.

Fission by Ozone of Trimethyl-γ-chloroallylammonium Chloride: Formation of Hydrogen Chloride, Carbon Monoxide, and Betaine.—The chloride (5 g.), dissolved in *pure* acetic acid (30 c.c.), was treated with ozonised oxygen for 48 hours, during which the crystalline ozonide-salt was precipitated. The mixture was boiled with water (100 c.c.) and the evolved gas was passed through a solution of *p*-nitrophenylhydrazine acetate contained in a bulb attached to the top of the reflux: no *p*-nitrophenylhydrazone was obtained. The solution contained free hydrochloric acid, since it contained chloride ions and was acid to Congo-red. It was evaporated and the base converted into its picrate, which had m. p. 183° and was identified

as betaine picrate by analysis and direct comparison (Found: C, 38·1; H, 4·2. Calc.: C, 38·2; H, 4·1%).

Fission by Ozone of Trimethyl-α-ethoxyallylammonium Acetate: Formation of Formaldehyde and Trimethylethoxyaldehydomethylammonium Salts.—The formation and the decomposition of the ozonide were carried out in acetic acid as above. After a test portion had been distilled for the identification of formaldehyde, the liquid was evaporated and the residue treated with aqueous sodium picrate. *Trimethylethoxyaldehydomethylammonium picrate*, which was thus obtained, separated from moist ethyl alcohol in prisms, m. p. 168° (Found: C, 41·9; H, 5·0; OEt, 11·8. $C_{13}H_{18}O_9N_4$ requires C, 41·7; H, 4·9; OEt, 12·0%). We were unable to obtain a semicarbazone salt, but found that the above picrate slowly neutralised one equivalent of alkali hydroxide in dilute solution.

Trimethylhydroxyaldehydomethylammonium Salts.—The above ethoxyaldehydo-salt was warmed with concentrated hydrochloric acid, and the excess of acid evaporated. The *picrate* obtained from the residue crystallised from water in prisms, m. p. 182—184° (Found: C, 38·8; H, 4·2. $C_{11}H_{14}O_9N_4$ requires C, 38·1; H, 4·0%).

Fission by Ozone of Trimethyl-α-hydroxyallylammonium Acetate.—The experiment being carried out as in the case of the corresponding α-ethoxy-salt, the products were formaldehyde and the preceding hydroxyaldehydo-salt.

Fission by Ozone of Triethyl-α-ethoxyallylammonium Acetate.—The decomposition was conducted as described for the trimethyl analogue, and the basic fraction treated with sodium picrate; the products were formaldehyde and *triethylethoxyaldehydomethylammonium picrate*, which crystallised from absolute ethyl alcohol in long prisms, m. p. 110—111° (Found: C, 46·1; H, 5·9. $C_{16}H_{24}O_9N_4$ requires C, 46·2; H, 5·8%).

Triethylhydroxyaldehydomethylammonium Salts.—The *picrate* was obtained as prisms, m. p. 195—196°, from the corresponding ethoxy-salt by hydrolysis with hydrochloric acid, and was crystallised from dilute alcohol (Found: C, 43·7; H, 5·3. $C_{14}H_{20}O_9N_4$ requires C, 43·3; H, 5·2%). It is sparingly soluble in absolute alcohol.

Fission by Ozone of Triethyl-α-hydroxyallylammonium Acetate.—The decomposition was carried out as in the case of the ethoxyallyl-salt; the products were formaldehyde and the preceding hydroxyaldehydo-salt.

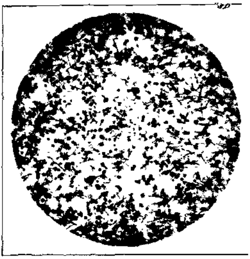
We wish to record our thanks to the Chemical Society and the Royal Society for grants from which this work received considerable assistance.

THE UNIVERSITY, LEEDS. [*Received, November 19th, 1928.*]

FIG. 1.

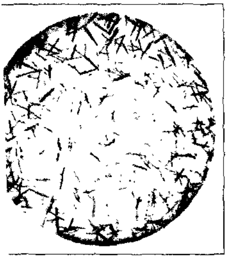
a *Dioxide* (*labile*) (× 12).

FIG. 2.



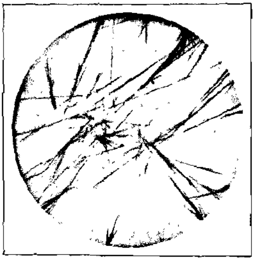
a-*Dioxide* (*labile and stable*) (× 12).

FIG. 3.



a-*Dioxide* (*stable*) (× 12).

FIG. 4.



β-*Dioxide* (× 12).

[*To face p.* 15.]

III.—*Stereoisomerism of Disulphoxides and Related Substances. Part IV. Di- and Tri-sulphoxides of Trimethylene Trisulphide.*

By Ernest Vere Bell and George Macdonald Bennett.

Stereochemical theory indicates the possibility of two disulphoxides and two trisulphoxides derived from the cyclic trimethylene trisulphide. A crystalline trisulphoxide was prepared by Hinsberg (*J. pr. Chem.*, 1912, **85**, 337), who subsequently announced that the small, almost insoluble residue rejected in its purification was an isomeric trioxide (*ibid.*, 1914, **89**, 547). On the other hand, Fromm and Schultis (*Ber.*, 1923, **56**, 937) contended that the latter substance is not a true sulphoxide of trimethylene trisulphide but a compound of high molecular weight. A single crystalline disulphoxide was also isolated by Hinsberg (*J. pr. Chem.*, 1913, **88**, 49). We have reinvestigated the oxidation of pure trimethylene trisulphide and have isolated a monoxide, two dioxides and two trioxides, and the relationships which exist between them lead to an exact determination of their configurations.

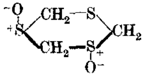
The practical problem involved was solved by the method of oxidation described in Part II (J., 1928, 86). Fromm and Ungar (*Ber.*, 1923, **56**, 2286) had reported that the oxidation of dithian with one molecular proportion of hydrogen peroxide yielded its dioxide, some of the sulphide being unchanged. It appeared to us, nevertheless, that a monoxide should be capable of existence and must occur as an intermediate in this oxidation. The carefully controlled oxidation of dithian did, in fact, yield the monoxide. When trimethylene trisulphide was oxidised by this method, it also furnished a *monoxide*. This was subjected to further cautious oxidation, and by fractional crystallisation of the product from water three distinct crystalline substances were isolated all having the composition and molecular weight of a dioxide of the parent sulphide. There had, however, been indications that two of these substances were polymorphic forms of one chemical individual. This polymorphism was confirmed by the direct interconversion of the two forms. Sidgwick's test (J., 1915, **107**, 672) was applied and the results indicate that the three substances are a pair of polymorphic forms of an *α-disulphoxide* and an entirely distinct β-disulphoxide. Crystals of these substances suitable for goniometry have not been obtained, but their character is illustrated by photomicrographs of the α-dioxide (Fig. 1, labile form; Fig. 2, labile form partly converted into the stable form; Fig. 3, stable form) and the β-dioxide (Fig. 4).

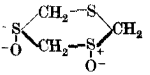
When these dioxides were subjected to further oxidation, each yielded the α-trioxide, but oxidation of the β-dioxide gave in addition a second (β)-*trioxide* more than ten times as soluble in water as its isomeride. A careful search showed that none of this substance was present in the product of oxidation of the α-dioxide.

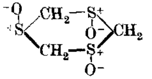
It is clear that Hinsberg's dioxide is identical with our β-dioxide and that his crystalline trioxide is identical with our α-trioxide. The sparingly soluble "trioxide" is entirely different from our β-trioxide and therefore our results confirm the criticism of Fromm and Schultis.

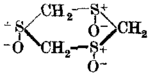
Gentle reduction of any of the five oxidation products we describe yields the parent trisulphide.

A consideration of the results of oxidising the two dioxides shows that the α-dioxide must have the *trans*-configuration (I) and the β-dioxide the *cis*-configuration (II).

(I.) 

 (II.)

(III.) 

 (IV.)

For the addition of an oxygen atom to (I) must yield a single trioxide (III) whether the added atom be above or below the plane of the ring. But, on the other hand, the *cis*-configuration (II) must on oxidation produce a mixture of isomerides having the *cis-trans*-(III) and the *cis-cis*-configuration (IV). It also follows that the α-trioxide, being the common oxidation product of both dioxides, is represented by (III), and the β-trioxide has the *cis-cis*-configuration (IV).

The genetic relationships between these substances thus lead to an absolute proof of their stereochemical structures. This is of great interest at a time when the possibility of the closure of a ring between groups in the *trans*-position, the new conception of the Beckmann transformation, and complications of the type of the Walden inversion introduce an uncertainty into many similar stereochemical problems. It is reassuring to notice that the configurations deduced above are in agreement with those which might have been tentatively assumed from the solubility relations of the isomerides: the *cis* (β)-dioxide is more soluble in water than its *trans* (α)-isomeride and the *cis-cis* (β)-trioxide much more so than the *cis-trans* (α)-isomeride. This lends considerable support to the

allocation of formulæ to the two dioxides of dithian which we made in Part I (J., 1927, 1799).

The configurative relationships between the di- and tri-sulphoxides described above are closely analogous to those involved in the work of Perkin and Robinson (J., 1921, **119**, 1392) on ethyl dibromoadipate and still more in that of Ing and Perkin (J., 1925, **127**, 2387) on the dibromoglutaric esters. The latter authors found that two stereoisomeric methyl αα′-dibromoglutarates, each by a malonic ester condensation, yielded two isomeric *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylic esters. One of these esters by hydrolysis and loss of carbon dioxide gave a single *trans-cyclo*butane-1 : 2 : 3-tricarboxylic acid, whereas the other yielded a mixture of this acid with its *cis*-isomeride. The principle of Ing and Perkin which we have utilised should have led to a determination of the configuration of the original dibromo-esters, but the results point to a partial interconversion of stereoisomerides and are therefore inconclusive. No configurative changes of this type can have occurred in our experiments, for the trimethylene trisulphide ring remained intact throughout and the reactions involved are practically quantitative at laboratory temperature.

The large number of analyses used to control the fractional crystallisations involved in this investigation would have been almost impossible from the point of view of either time or cost but for the macro-modification of Pregl's determination of sulphur which we have recently described (J., 1928, 3192).

EXPERIMENTAL.

Oxidation of Trimethylene Trisulphide to a Monoxide.—Carefully purified acetone (4 l.) and trimethylene trisulphide (recrystallised successively from glacial acetic acid and xylene; 39·2 g.) were stirred together at 40° while a solution of hydrogen peroxide (35·8 g. of 27% strength in 400 c.c. of acetone) was run in drop by drop during 6 hours. After 12 hours, the solvent was evaporated and the solid residue was extracted with hot water, 7 g. of trimethylene trisulphide remaining undissolved. The material recovered from the water by evaporation was further freed from dioxide by extraction of the monoxide with absolute ethyl alcohol. This substance (14 g.) was finally recrystallised several times from water. *Trimethylene trisulphide monoxide* forms colourless needles with a straight extinction and a high double refraction, m. p. 187° (Found: S, 62·3. $C_3H_6OS_3$ requires S, 62·3%). It is easily soluble in warm but less soluble in cold water or acetic acid, and moderately easily soluble in ethyl alcohol or acetone.

Oxidation of the Monoxide to the Isomeric Dioxides.—The mon-

oxide (30·7 g. collected from three of the above-described oxidations), dissolved in glacial acetic acid (750 c.c.), was kept stirred at room temperature during the addition, over a period of 6 hours, of the calculated amount of hydrogen peroxide (25·2 g. of 27% strength in 375 c.c. of acetic acid). After 12 hours, the acetic acid was distilled under reduced pressure below 50°. The crude oxidation product was separated by a long process of fractional crystallisation from water into the labile and stable forms of the α-dioxide and the β-dioxide.

α-Trimethylene trisulphide dioxide (yield, 6 g.) decomposes at 220—280° and is dimorphous. The *labile* form crystallises from water in almost square plates with a high double refraction and an extinction angle of 16° (Found: C, 21·0; H, 3·6; S, 56·35. $C_3H_6O_2S_3$ requires C, 21·2; H, 3·5; S, 56·5%). The *stable* form crystallises from water in stout monoclinic prisms with an extinction angle of 35° (Found: C, 20·8; H, 3·7; S, 56·6%. *M*, cryoscopic in water, 174, 206. $C_3H_6O_2S_3$ requires *M*, 170). When this form is recrystallised from water, it often, but not always, separates in the labile form. The latter, on standing in contact with the solution from which it has crystallised, changes more or less rapidly into the stable form.

The β-trimethylene trisulphide dioxide (yield, 4 g.) decomposes at 200—215° (Found: C, 21·2; H, 3·5; S, 56·4; *M*, 153, 174). It crystallises from water in bundles of pointed needles having an extinction angle of 32°. Both α- and β-dioxides are sparingly soluble in most organic solvents, but soluble in acetic acid.

Solubilities of the Isomerides and Proof of the Polymorphism.—The solubilities of the stable form of the α-dioxide and of the β-dioxide were determined by evaporation of a weighed sample of an aqueous solution which had been stirred with the solid for 3 hours in a thermostat at 25·0°. 100 G. of water at 25° dissolve 1·70 g. of the α-dioxide, and 4·53 g. of the β-dioxide.

The following results were obtained by Sidgwick's cryoscopic method with water as solvent:

Depression with α-dioxide (labile)	0·087°
,, ,, α-dioxide (stable)	0·073
,, ,, α-dioxide (labile and stable)	0·083
,, ,, β-dioxide	0·226
,, ,, β-dioxide and α-dioxide (stable)	0·270

These figures show that the two forms of α-dioxide are polymorphic and the β-dioxide is isomeric.

Oxidation of the Isomeric Dioxides.—The α-dioxide (2·45 g.), dissolved in acetic acid (100 c.c.), was stirred at laboratory temperature while, during 1 hour, 50 c.c. of a solution of hydrogen peroxide (38·6 g. of 25·4% strength in 1 l. of acetic acid) were added. After 12 hours, the acetic acid was distilled under diminished pressure. The residue (yield, nearly quantitative) consisted of the single

substance α-trimethylene trisulphoxide and crystallised from water in bundles of radiating minute prisms with oblique extinction, decomp. 230—280° (Found: S, 51·2. Calc. for $C_3H_6O_3S_3$: S, 51·6%). It is insoluble in alcohol or acetone, and sparingly soluble in acetic acid or water.

The β-dioxide was oxidised in a precisely similar manner. The crude product (2·9 g.) was separated by fractional crystallisation from water into the α-trioxide described above (Found: S, 51·5%) and the *β-trimethylene trisulphoxide*, which crystallised from water in minute separate prisms with an extinction angle of 32°, decomp. 220—260° (Found: S, 52·0%). This substance is sparingly soluble in alcohol, acetone, and other organic solvents and moderately easily solnble in acetic acid or cold water.

Solubilities of the Isomeric Trioxides in Water.—The solubilities, determined as before, are: 100 g. of water at 25·0° dissolve 0·134 g. of the α-trioxide and 1·437 g. of the β-trioxide.

Reduction of the Sulphoxides.—The α- and β-dioxides and the α- and β-trioxides were each reduced by means of zinc dust and dilute hydrochloric acid to the parent trimethylene trisulphide, which was identified by its melting point and that of a mixture with the trisulphide.

Oxidation of Trimethylene Trisulphide to the Trioxide.—The finely powdered trisulphide was kept for a week with hydrogen peroxide (3 mols.) in acetic acid, and the solution filtered. The solid residue, recrystallised from water, yielded the pure α-trioxide (Found: S, 51·1%). The acetic acid was removed from the solution by distillation in steam and evaporation on the steam-bath. There remained a mixture of the disulphoxides (Found: S, 55·3%).

Examination of Hinsberg's Supposed Isomeric Form of Trimethylene Trisulphide.—Trimethylene trisulphide was heated with hydriodic acid (*d* 1·7) for 1½ hours at 100°. Water was added, and the product was filtered off and washed successively with water, thiosulphate, and again with water. It was a pale brown, crystalline substance, m. p. 247° (decomp.), and evolved a trace of hydrogen sulphide above its melting point. Recrystallisation converted it into the ordinary trisulphide of m. p. 216°. The determination of its molecular weight was therefore not feasible. The composition [Found: I, 0·9; C, 24·6, 24·7; H, 4·6, 4·4; S (as $BaSO_4$), 66·6. CH_2S requires C, 26·1; H, 4·35; S, 69·55%], after allowance has been made for the small amount of iodine present, is still different from that of a polymeride of CH_2S. There would appear to be some oxygen in the substance.

THE UNIVERSITY, SHEFFIELD. [Received, November 30th, 1928.]

IV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part V.*

By Edward de Barry Barnett and Norman Frederick Goodway.

The formation of an alkyl or aryl dihydroanthranol (II) and the formation from it of the *meso*-alkyl or *meso*-aryl anthracene (III) by transannular loss of water by the action of a Grignard solution on an anthrone (I) (for references to earlier work see Part II, J., 1927, 1725; also Cook, J., 1928, 2798) are profoundly influenced by substituents both in the *meso*-positions and also in the side rings.

$$\text{(I.)}\ X{<}\begin{matrix}CO\\ \\ CH_2\end{matrix}{>}X \qquad X{<}\begin{matrix}R{\cdot}C{\cdot}OH\\ \\ CH_2\end{matrix}{>}X\ \text{(II.)} \qquad X{<}\begin{matrix}R{\cdot}C\\ |\\ CH\end{matrix}{>}X\ \text{(III.)}$$

In the case of 1 : 5-dichloroanthrone the method leads to satisfactory yields of the *meso*-methyl-, -ethyl-, and -benzyl-anthracene, but breaks down with the other magnesium alkyl halides (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 2863; 1927, **60**, 2353). 1 : 5-Dichloro-9-methylanthrone (Barnett and Cook, *Ber.*, 1928, **61**, 314), 1 : 5-dichloro-9-benzylanthrone (Barnett and Cook, J., 1928, 566), and 1 : 5-dichloro-9-phenylanthrone (Barnett, Cook, and Wiltshire, J., 1927, 1724) behave in much the same way, but it seemed possible that better results might be obtained with 1 : 5-*dichloro-9-benzhydrylanthrone* (IV) (readily obtained by boiling 1 : 5-dichloroanthrone with benzhydryl chloride and caustic alkali), as this shows hardly any tendency to enolise to the anthranol; and as the resulting dihydroanthranol (V) might be expected to lose the benzhydryl group easily (compare the conversion of tribenzyldihydroanthranol into 9 : 10-dibenzylanthracene; Barnett and Cook, J., 1928, 566: and the facile reduction of dianthrone to anthrone; Barnett and Matthews, J., 1923, **123**, 380), this would permit of an indirect method of preparing the higher alkyl dichloroanthracenes.

These expectations have been only partly fulfilled, as, although 1 : 5-dichloro-9-benzhydrylanthrone does give crystalline dihydroanthranols when treated with a Grignard solution, the yields obtained are very poor (about 5%) except in the cases of the methyl, benzyl, and phenyl compounds.

$$C_6H_3Cl{<}\begin{matrix}CO\\ \\ H{\cdot}C{\cdot}CHPh_2\end{matrix}{>}C_6H_3Cl \qquad C_6H_3Cl{<}\begin{matrix}R{\cdot}C{\cdot}OH\\ \\ H{\cdot}C{\cdot}CHPh_2\end{matrix}{>}C_6H_3Cl \qquad C_6H_3Cl{<}\begin{matrix}HO{\cdot}C{\cdot}R\\ \\ H{\cdot}C{\cdot}CHPh_2\end{matrix}{>}C_6H_3Cl$$

(IV.) (V.) (VI.)

The loss of benzhydrol takes place even more easily than would be expected, as brief heating on the water-bath with acetic acid con-

taining a little hydrochloric acid resulted in the production of methyl-, ethyl-, benzyl-, and phenyl-dichloroanthracene. That transannular loss of benzhydrol takes place in preference to transannular loss of water suggests configuration (V) rather than configuration (VI) for the dihydroanthranol, and benzhydryldichloroanthrone itself, on reduction both in acid and in alkaline solution, loses its benzhydryl group and passes into dichloroanthracene, possibly owing to transannular loss of benzhydrol from the dihydroanthranol which is probably first formed during the reduction.

Phenylbenzhydryldichlorodihydroanthranol (V, R = Ph) undergoes change on thermal treatment in boiling xylene and passes into an isomeric substance. This may be the geometrical isomeride represented by (VI), or the isomerism may be due to the non-coplanar arrangement of the anthracene ring system, of which evidence has recently been obtained by Schlenk (*Annalen*, 1928, **463**, 1). As both isomerides undergo facile transannular loss of benzhydrol with formation of 1 : 5-dichloro-9-phenylanthracene, the balance of evidence is rather in favour of the latter type of isomerism; at present, however, methods of obtaining definite proof are not available.

EXPERIMENTAL.

1 : *5-Dichloro-9-benzhydrylanthrone* (IV).—1 : 5-Dichloroanthrone (20 g.), potassium hydroxide (200 c.c. of 20% solution), and crude benzhydryl chloride (40 c.c.) were boiled under reflux until the liquid, which at first was almost black, became pale in colour (about 30 minutes). The cooled product was washed with water and then triturated with a little cold ether in order to remove resinous by-products. After recrystallisation from methyl ethyl ketone or ethyl acetate it formed colourless, glistening crystals, m. p. 191°. It gave scarcely any colour with boiling alcoholic alkali and all attempts to obtain an acetate of the corresponding anthranol failed (Found : C, 75·3; H, 4·3. $C_{27}H_{18}OCl_2$ requires C, 75·5; H, 4·2%).

The yield of the above compound does not exceed 50% owing to the simultaneous formation of a yellow, resinous substance. This was recovered from the ethereal washings but could not be made to crystallise.

Reduction of 1 : *5-Dichloro-9-benzhydrylanthrone.*—Reduction was carried out (*a*) with zinc dust and caustic potash in alcoholic solution, (*b*) with zinc dust and hydrochloric acid in acetic acid solution. In each case 1 : 5-dichloroanthracene resulted and was identified by direct comparison with an authentic sample, and in each case the liquor smelt strongly of diphenylmethane.

Action of Grignard Reagents on 1 : *5-Dichloro-9-benzhydrylanthrone.*—In each case the finely powdered anthrone (4·3 g.; 0·01 mol.) was

added to an ethereal Grignard solution prepared from 0·72 g. (0·03 mol.) of magnesium, and after being kept for 30 minutes in the freezing mixture and for 4—5 hours at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium chloride. In the cases of the methyl, benzyl, and phenyl compounds the greater part of the resulting dihydroanthranol (V) was obtained directly in the solid state, and further amounts were obtained by evaporation of the washed ethereal solution. In all other cases the product was completely and easily soluble in ether and evaporation of the washed solution resulted in a viscous oil from which small quantities of the crystalline dihydroanthranol were obtained by cautious treatment with aqueous acetone, keeping over-night in contact with the solvent frequently being necessary. In these cases the yield did not exceed 5%. Purification of the crude dihydroanthranol was effected by recrystallisation from aqueous acetone, and the resulting colourless crystals were dried in the steam-oven before analysis.

No dihydroanthranol could be isolated when benzhydryldichloroanthrone was treated with magnesium *p*-anisyl bromide, magnesium *o*-tolyl bromide, or magnesium α-naphthyl bromide, the only solid product being the unchanged anthrone even when the preparation was kept over-night before being poured on ice and ammonium chloride.

In the following table the melting points and analytical data of the dihydroanthranols are recorded, the calculated figures being given in parentheses.

Alkyl or aryl group.	M. p.	Cl, %.	Alkyl or aryl group.	M. p.	Cl, %.
Me	160°	16·3 (16·0)	*iso*-C_4H_9	212°	14·6 (14·6)
Et	140	15·7 (15·5)	*iso*-C_5H_{11}	193	14·3 (14·2)
$Pr^α$	185	15·0 (15·0)	CH_2Ph..................	206	13·8 (13·6)
$Pr^β$	170	15·0 (15·0)	Ph (recrystallised from methyl ethyl ketone and rapidly from toluene)	259	13·9 (14·0)
n-C_4H_9.........	182	14·5 (14·6)			

The methyl, ethyl, benzyl, and phenyl compounds mentioned above, when heated on the water-bath with acetic acid containing a little hydrochloric acid, passed very easily into the corresponding alkyl (or phenyl) anthracene (identified by direct comparison with authentic samples). The amounts of the other dihydroanthranols were too small to allow their behaviour to be examined.

iso-1 : 5-Dichloro-9-phenyl-10-benzhydryl-9 : 10-dihydroanthranol (V or VI, R = Ph).—The phenyldihydroanthranol included in the foregoing table maintained a constant melting point so long as recrystallisation was effected from a solvent with a low boiling point (methyl ethyl ketone or toluene). Recrystallisation from xylene,

however, led to a progressive rise in melting point, and when 1·5 g. of the substance were boiled under reflux with 20 c.c. of xylene for 4 hours the product obtained melted at 271° and showed no change in melting point on further thermal treatment (Found: Cl, 14·2. $C_{33}H_{24}OCl_2$ requires Cl, 14·0%). This product, on treatment on the water-bath with acetic acid containing hydrochloric acid, passed easily into 1 : 5-dichloro-9-phenylanthracene.

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SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C. 3. [*Received, November 26th, 1928.*]

V.—*Researches in the Menthone Series. Part VI. The Crystallisation of Menthylamines with Optically Active Acids.*

By JOHN READ, CATHERINE CASSELS STEELE, and PETER GEORGE CARTER.

IT has been shown (J., 1926, 2209; 1927, 2168) that *l*-, *d*-*neo*-, *d*-*iso*-, and *d*-*neoiso*-menthylamine may be prepared easily from *l*-piperitone, and the externally compensated forms of the first three of these stereoisomeric bases from *dl*-piperitone (J., 1926, 2223). So far, however, no convenient method of obtaining the enantiomerides of the above active forms has been described; for although *d*-piperitone and *d*-menthol might serve for the purpose (J., 1926, 2214; *J. Soc. Chem. Ind.*, 1927, **46**, 871), these substances may be secured only with considerable difficulty and in small amounts.

As a result of an examination of possible methods for the optical resolution of *dl*-, *dl*-*neo*-, and *dl*-*iso*-menthylamine with the aid of optically active acids, we are now able to describe satisfactory processes for the preparation in quantity of *d*-menthylamine and *l*-*neo*-menthylamine. The first of these results may be regarded as particularly important, since it not only furnishes a new optically active base of unusual interest but also opens up a new route to *d*-menthol, which may be obtained by the interaction of *d*-menthylamine with nitrous acid.

dl-Menthylamine and *dl*-*neo*-menthylamine were resolved by fractionally crystallising the hydrogen *d*-tartrates in the usual way; in each instance the salt containing the desired form of the

base (*dAdB* and *dAlB*, respectively) was fortunately the less soluble of the two diastereoisomerides. *dl-iso*-Menthylamine was not resolved when treated in a similar way. Altogether, four methods of resolution were applied to each of the three externally compensated bases under consideration, the salts examined being the *d*(or *l*)-α-bromocamphor-π-sulphonates, *d*(or *l*)-camphor-10-sulphonates, and the normal and hydrogen *d*-tartrates. Complete resolution was achieved only in the two instances noted, but a study of the behaviour of the other salts concerned has disclosed results of considerable general interest. The appended table contains a summary of the molecular rotatory powers in dilute aqueous solution of the optically pure salts, prepared in the majority of instances by mixing equivalent weights of the optically active acid and base and recrystallising the product. The values of $[M]_D$ for the acidic and basic ions in dilute aqueous solution are taken as follows: α-bromocamphor-π-sulphonic acid ± 279° (J., 1910, **97**, 2201), camphor-10-sulphonic acid ± 50° (J., 1910, **97**, 2214), *d*-tartaric acid + 42° for the acid salts (Meyer und Jacobson, "Lehrbuch der organischen Chemie," 1913, I, ii, 666), *l*-menthylamine − 70°, *d-neo*-menthylamine + 41°, and *d-iso*-menthylamine + 45° (J., 1927, 2169). The observed value for each salt is stated immediately below the value calculated for it from the data just quoted.

TABLE I.

Values of $[M]_D$, *calculated and observed, for salts of certain menthylamines with optically active acids in dilute aqueous solution.*

Acid.	*l*-Base.	*d-neo*-Base.	*d-iso*-Base.
d-α-Bromocamphor-π-sulphonic, calc.	+209°	+320°	+324°
obs.	+207	+341	+396
l-α-Bromocamphor-π-sulphonic, calc.	−349	−238	−234
obs.	−348	−230	−249
d-Camphor-10-sulphonic, calc.	− 20	+ 91	+ 95
obs.	−20·5*	+ 93	+ 95
l-Camphor-10-sulphonic, calc.	−120	− 9	− 5
obs.	−112	± 0	± 0
d-Tartaric (acid salt), calc.	− 28	+ 83	+ 87
obs.	− 25	+ 84	+ 98
	d-Base.	*l-neo*-Base.	
d-Tartaric (acid salt), calc.	+112	+ 1	
obs.	+113	± 0	

* Tutin and Kipping, J., 1904, **85**, 70.

As it might be unjustifiable to assume practically complete ionisation on the part of the normal tartrates, the values for these salt have not been included. No marked divergence from the calculated values is apparent in this list except among the α-bromocamphor

e most pronounced discrepancies ar

shown by salts of the type *d*A*d*B; similar instances of abnormalities when the constituent ions are of the same sign of rotatory power have been pointed out by Pope and Read (J., 1912, **101**, 775).

The tartrates and camphor-10-sulphonates noted above gave essentially constant optical rotatory powers in dilute aqueous solution, but with the α-bromocamphor-π-sulphonates considerable fluctuations were observed in the optical activity. Sensibly identical values for two consecutive preparations were rarely observed, and changes occurred upon evaporating or recrystallising particular specimens of these salts. This behaviour is probably to be referred to the occurrence of dynamic isomerism on the part of the acid, similar observations having been made by Kipping and his collaborators in studying its salts with hydrindamine (J., 1900, **77**, 872), benzylhydrindamine (J., 1901, **79**, 435), β-methylhydrindamine (J., 1903, **83**, 922), and *l*-menthylamine (J., 1904, **85**, 68; see also J., 1905, **87**, 632); salts of *d*-α-bromocamphor-10-sulphonic acid also have been shown to display corresponding changes in rotatory power (Pope and Read, J., 1914, **105**, 800). Such behaviour appears to be most noticeable when the acid is combined with a strong primary base, and the optical resolution of such bases is therefore liable to be complicated by the formation of α- and β-salts.

Upon fractional crystallisation of the salts of the three above-mentioned externally compensated menthylamines with *d*-α-bromocamphor-π-sulphonic acid, the rotatory powers of successive fractions oscillated irregularly and afforded no satisfactory indication of the rotatory power of the contained base (compare Table II*a*); in none of these instances was it possible to achieve more than a partial resolution of the base. This result was to be anticipated, and an explanation may be found on the lines indicated above.

Unexpectedly, however, the *d*-camphor-10-sulphonates prepared from these externally compensated bases exhibited very similar irregularities in their optical rotations (compare Table II*b*), and it was not found possible to resolve any of the bases with the help of this acid. Since the *d*- and *l*-camphor-10-sulphonates of the pure optically active bases gave constant and normal optical rotations (Table I), it does not appear possible in this case to ascribe the observed variations to tautomerism of the acid; moreover, no change in the rotatory power of a particular specimen of such a salt was noticed upon evaporating its aqueous solution to dryness. Further experiments showed also that the optically active menthylamines do not undergo optical inversion when liberated from their salts. The explanation advanced above thus appears inadequate to account for the abnormal rotatory powers of the mixed diastereo-

isomeric salts obtained by combining d-camphor-10-sulphonic acid with a specific externally compensated menthylamine.

For the present, the abnormal behaviour described in this paper has prevented the complete optical resolution of any of the externally compensated menthylamines with the aid of camphor-10-sulphonic acid or α-bromocamphor-π-sulphonic acid; possibly, *however, more favourable results may attend* fractional crystallisation of the respective pairs of these diastereoisomeric salts from *hot solutions, or from solutions containing* small amounts of free acid or alkali.

EXPERIMENTAL.

Salts of Menthylamines.

1. *α-Bromocamphor-π-sulphonates.*—Equimolecular amounts of *l*-menthylamine hydrochloride and ammonium *l*-α-bromocamphor-π-sulphonate were dissolved in about ten times their weight of hot water, to which a little alcohol was added. On cooling, the solution deposited *l*-menthylamine *l*-α-bromocamphor-π-sulphonate in small prisms; after two recrystallisations from dilute alcohol, the salt * had m. p. 183—184°, $[\alpha]_D$ −74·7°, $[M]_D$ −348°. The rotatory power was practically unaffected by evaporating an aqueous solution of the salt to dryness. The salt dissolved readily in alcohol, chloroform, or acetone.

l-Menthylamine *d*-α-bromocamphor-π-sulphonate, prepared similarly, had m. p. 225°, $[\alpha]_D$ +44·4°, $[M]_D$ +207° (compare J., 1904, 85, 69, 71).

When *dl*-menthylamine hydrochloride (J., 1926, 2226) was mixed in the same way with ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.), a first fraction of the separation, forming about one-quarter of the total quantity possible, had $[M]_D$ +275°. Repeated crystallisation of this product yielded further fractions having values of $[M]_D$ which fluctuated irregularly between +223° and +324°. Similar values were exhibited by a large number of fractions deposited from the various mother-liquors. Results of the same general character were obtained when ethyl acetate was used as the solvent. The following values (Table II*a*) were found upon regenerating menthylamine hydrochloride from a series of these fractions.

* Unless *otherwise* stated, the following conditions hold for *all* optical rotatory powers quoted in this paper: the dry, anhydrous salt (*w* g.) was dissolved in water to form a solution having a concentration of approximately 1%, and the observation was made in a 2-dcm. tube at the ordinary temperature (about 15°). In order to economise space, the observed values of α are only quoted, as a rule, when they fall below 0·2°. The respective values of *M* for menthylamine α-bromocamphor-π-sulphonate, camphor-10-sulphonate, normal tartrate, and hydrogen tartrate are 466, 387, 460, and 305.

TABLE II.

Molecular rotatory powers of salts derived from mixtures of l- *and* d-*menthylamine.*

$[M]_D$ of fraction.	$[M]_D$ of basic ion: Calc. (from salt).	$[M]_D$ of basic ion: Found (for hydrochloride).
(a) d-α-*Bromocamphor*-π-*sulphonates.*		
+205°	−73°	−14°
+225	−43	−10
+260	−18	± 0
+324	+46	+29
+312	+34	+35
(b) d-*Camphor*-10-*sulphonates.*		
+43	− 7	± 0
+31	−19	± 0
+33	−17	− 6
+50	± 0	− 9
+38	−12	± 0
(c) *Hydrogen* d-*tartrates.*		
+38	− 4	− 4
+35	− 7	− 6
+18	−24	−25
± 0	−42	−43

2. *Camphor*-10-*sulphonates.*—Equimolecular proportions of ammonium *l*-camphor-*10*-sulphonate and *l*-menthylamine hydrochloride were dissolved in about eleven times their weight of hot water; the crystalline separation of l-*menthylamine* l-*camphor*-10-*sulphonate*, which formed as the liquid cooled, was recrystallised from hot water, after which it had $[\alpha]_D$ − 28·9°, $[M]_D$ − 112°. The salt preserved this rotatory power when again recrystallised. It dissolved in alcohol and chloroform, and less readily in acetone, benzene, and ethyl acetate (Found: C, 61·4; H, 9·3. $C_{20}H_{37}O_4NS$ requires C, 62·0; H, 9·6%).

The salt formed by *dl*-menthylamine with *d*-camphor-10-sulphonic acid was prepared and fractionally crystallised from water in the manner outlined under (1) above. The first fraction had $[M]_D$ + 48°, and as a result of repeated fractional crystallisation specimens of salt were obtained with values of $[M]_D$ fluctuating irregularly between + 31° and + 60°. Similar fractions were deposited from the mother-liquors. Fractionation from ethyl acetate yielded equally indefinite results. The values observed on regenerating the base from a number of these fractions are summarised above (Table IIb).

3. *Normal Tartrates.*—*l*-Menthylamine (2 mols.) dissolved in ether was mixed with *d*-tartaric acid (1 mol.) dissolved in warm alcohol. A crystalline deposit of *l*-menthylamine *d*-tartrate separ-

ated as the solution cooled. It was readily soluble in water or alcohol, and slightly soluble in acetone or ethyl acetate; but recrystallisation was impracticable, owing to the tendency of the salt to pass into a syrup. In dilute aqueous solution it gave $[\alpha]_D - 24{\cdot}6°$, $[M]_D - 113°$.

When *dl*-menthylamine (2 mols.) was mixed with *d*-tartaric acid (1 mol.) in warm alcohol, a gummy salt was formed. This became crystalline when treated with small quantities of dry acetone, but efficient fractional crystallisation was impracticable. The purest fraction isolated had $[\alpha]_D + 13{\cdot}0°$, $[M]_D + 60°$, and this yielded optically impure *d*-menthylamine hydrochloride with $[M]_D + 15°$ (w 0·1990 g., $\alpha + 0{\cdot}16°$).

4. *Hydrogen Tartrates.*—A crystalline salt was readily obtained on mixing equimolecular proportions of *l*-menthylamine and *d*-tartaric acid in hot alcohol. After recrystallisation from hot water, *l*-menthylamine hydrogen *d*-tartrate had $[\alpha]_D - 8{\cdot}0°$, *$[M]_D - 25°$ (w 0·1990 g., $\alpha - 0{\cdot}16°$); it dissolved in alcohol, but not in acetone, chloroform, benzene, or ethyl acetate.*

Optical Resolution of dl-*Menthylamine.*—*dl*-Menthylamine hydrochloride (18·4 g., 1 mol.) was decomposed with sodium hydroxide solution, and the free base, isolated by means of ether, was dissolved in warm alcohol containing *d*-tartaric acid (14·4 g., 1 mol.). When the salt obtained after removal of the alcohol was fractionally crystallised from boiling water, the first (10·7 g.) and second (4·8 g.) fractions had $[M]_D + 101°$ and $+ 80°$, respectively. Two further recrystallisations of these fractions sufficed to give 36% of the theoretical yield of pure d-***menthylamine hydrogen*** d-***tartrate***, m. p. 168°, $[\alpha]_D + 37{\cdot}1°$, $[M]_D + 113°$, $[\alpha]_{5461} + 39{\cdot}1°$, $[M]_{5461} + 119°$ (Found: C, 54·5; H, 9·3. $C_{14}H_{27}O_6N$ requires C, 55·0; H, 8·7%). *d*-Menthylamine hydrochloride prepared from this salt had $[\alpha]_D + 36{\cdot}6°$, $[M]_D + 70°$. Salicylidene-*d*-menthylamine, m. p. 56—57°, $[\alpha]_D + 118°$ (c 0·75 in chloroform), showed the marked phototropic effect characteristic of salicylidene-*l*-menthylamine (J., 1926, 2234; 1927, 2174).

In conducting the above resolution it is advisable to seed the original solution with a crystal of pure *d*-menthylamine hydrogen *d*-tartrate. A final fraction obtained in the process displayed no appreciable optical activity when examined under the usual conditions; when decomposed, this yielded impure *l*-menthylamine hydrochloride having $[M]_D - 43°$. This and other specimens of the hydrochloride obtained from intermediate fractions displayed rotatory powers in approximate agreement with the calculated values (Table IIc).

Salts of neo*Menthylamines.*

1. *α-Bromocamphor-π-sulphonates.*—*d*-*neo*Menthylamine hydrochloride (J., 1926, 2217), having $[\alpha]_D + 21{\cdot}5°$ in 1% aqueous solution, was dissolved in hot water and mixed with ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.); the resulting separation of colourless prisms consisted of *d*-*neo*menthylamine *d*-α-bromocamphor-π-sulphonate, m. p. 166·5°, $[\alpha]_D + 70{\cdot}8°$, $[M]_D + 330°$. A second preparation, made from the same specimens, had $[\alpha]_D + 73{\cdot}3°$, $[M]_D + 341°$. d-neo*Menthylamine* l-*α-bromocamphor-π-sulphonate*, prepared similarly, separated from water in long soft needles, m. p. 171°, $[\alpha]_D - 49{\cdot}3°$, $[M]_D - 230°$ (Found: C, 49·9; H, 7·4. $C_{20}H_{36}O_4NBrS$ requires C, 51·5; H, 7·8%).

The crystalline deposit obtained on mixing hot aqueous solutions of *dl*-*neo*menthylamine hydrochloride (2 mols.; J., 1926, 2227) and ammonium *d*-α-bromocamphor-π-sulphonate (1 mol.) had $[M]_D + 283°$; when the salt was recrystallised twice from dilute alcohol the molecular rotation changed through $[M]_D + 291°$ to $[M]_D + 318°$. The last fraction, m. p. 171°, when decomposed gave optically impure *l*-*neo*menthylamine hydrochloride having $[M]_D - 6°$. On adding a second molecular proportion of the ammonium salt to the original filtrate, a first fraction was deposited having $[M]_D + 287°$; the final fraction, having $[M]_D + 163°$, yielded optically impure *d*-*neo*menthylamine hydrochloride with $[M]_D + 9°$.

2. *Camphor*-10-*sulphonates.*—*d*-*neo*Menthylamine *d*-camphor-10-sulphonate, prepared by mixing equivalent weights of the acid and base in alcohol, separated from ether–light petroleum in clusters of small, transparent prisms, m. p. 180°, $[\alpha]_D + 24{\cdot}0°$, $[M]_D + 93°$. *l*-*neo*Menthylamine *l*-camphor-10-sulphonate crystallised from the same solvent in long prisms, m. p. 152°, $[M]_D \pm 0°$. No change was observed in these rotatory powers upon recrystallising the salts.

The salt obtained by mixing equimolecular weights of *d*-camphor-10-sulphonic acid and *dl*-*neo*menthylamine in warm alcohol was fractionally crystallised from ether–light petroleum. A series of fractions exhibited values of $[M]_D$ which fluctuated irregularly between + 75° and + 44°; the specimens of *neo*menthylamine hydrochloride prepared from these two limiting fractions had $[M]_D + 4°$ and $\pm 0°$, respectively.

3. *Normal Tartrates.*—*d*-*neo*Menthylamine *d*-tartrate crystallised from acetone–methyl alcohol in clusters of colourless needles, m. p. 180°, $[\alpha]_D + 25{\cdot}0°$, $[M]_D + 115°$.

When evaporated on the water-bath, an alcoholic solution of *dl*-*neo*menthylamine (2 mols.) and *d*-tartaric acid (1 mol.) yielded a crystalline mass, which was fractionally crystallised from acetone-methyl alcohol. After three recrystallisations, the molecular

rotation changed from $[M]_D$ + 86° through + 136° to + 124° The last fraction yielded optically impure *d-neo*menthylamine hydrochloride, with $[M]_D$ + 31°. A fraction having $[M]_D$ + 89° gave impure *l-neo*menthylamine hydrochloride, with $[M]_D$ − 18°.

4. *Hydrogen Tartrates.*—*d-neo*Menthylamine hydrogen *d*-tartrate crystallised from acetone–methyl alcohol in small, colourless prisms m. p. 179°, $[\alpha]_D$ + 27·4°, $[M]_D$ + 84°.

Optical Resolution of dl-neo*Menthylamine.*—Hot alcoholic solutions of *dl-neo*menthylamine (1 mol.) and *d*-tartaric acid (1 mol. were mixed, and the solvent was removed. Three recrystallisations of the resultant crystalline mass from acetone–methyl alcohol (1 : 1) furnished a pure specimen of *l-neo*menthylamine hydrogen *d*-tartrate, m. p. 188°; 0·2074 g. made up to 20 c.c. with water gave no appreciable optical rotation when examined in a 2-dcm tube in sodium light. *l-neo*Menthylamine hydrochloride prepared from this salt had $[\alpha]_D$ − 20·2°, $[M]_D$ − 39°. Salicylidene-*l-neo*menthylamine had m. p. 99°, $[\alpha]_D$ − 31·3° (*c* 0·33 in chloroform compare J., 1926, 2219).

Pure *d-neo*menthylamine hydrogen *d*-tartrate could not be isolated, but an impure fraction from the mother-liquors, having $[M]_D$ + 67°, yielded a specimen of optically impure *d-neo*menthylamine hydrochloride with $[M]_D$ + 25°.

Salts of iso*Menthylamines.*

1. *α-Bromocamphor-π-sulphonates.*—A hot aqueous solution of a mixture of equimolecular amounts of *d-iso*menthylamine (J., 1926 2221) and ammonium *d*-α-bromocamphor-π-sulphonate deposited upon cooling a mass of long slender needles of d-iso*menthylamine* d-*α-bromocamphor-π-sulphonate.* Repeated recrystallisation of this salt from boiling water yielded specimens for which the values of $[M]_D$ varied irregularly from + 396° to + 295° (Found : C, 51·1 H, 8·3. $C_{20}H_{36}O_4NBrS$ requires C, 51·5; H, 7·8%).

*d-iso*Menthylamine *l*-α-bromocamphor-π-sulphonate crystallised from boiling water in small prisms, m. p. 206° (decomp.). The values of $[M]_D$ for this salt showed variations similar to those observed for the diastereoisomeride, changing from − 201° through − 249° to − 212°.

Upon attempting the optical resolution of *dl-iso*menthylamine (J., 1925, 127, 2782; 1926, 2230) with the aid of ammonium *d*-α-bromocamphor-π-sulphonate, in the manner described above for *dl-neo*menthylamine, fractions of salt were obtained with values of $[M]_D$ ranging from + 263° to + 290°; the specimens of *iso*menthylamine hydrochloride prepared from these fractions were almost optically inactive, the highest rotatory power observed

being $[M]_D$ + 9°, for a hydrochloride from a fraction of salt having $[M]_D$ + 268°.

2. *Camphor*-10-*sulphonates*.—*d*-*iso*Menthylamine *d*-camphor-10-sulphonate, prepared from the free acid and base, crystallised from ethyl acetate in clusters of hard prisms, m. p. 180°, $[\alpha]_D$ + 24·6°, $[M]_D$ + 95°. *d*-*iso*Menthylamine *l*-camphor-10-sulphonate crystallised from ethyl acetate in soft needles, m. p. 188°, $[M]_D$ ± 0°. The *rotatory powers of both these salts remained unaltered on* further crystallisation.

Equimolecular amounts of *dl*-*iso*menthylamine and *d*-camphor-10-sulphonic acid were mixed in hot alcohol and the solvent was removed. Upon fractionation of the resultant crystalline mass from ethyl acetate, the molecular rotatory powers of the various fractions oscillated in an irregular manner between + 32° and + 51°; all the specimens of *iso*menthylamine hydrochloride prepared from these fractions were optically inactive in aqueous solution (*c* 3·5).

3. *Normal Tartrates*.—Hot alcoholic solutions of *d*-*iso*menthylamine (2 mols.) and *d*-tartaric acid (1 mol.) were mixed and evaporated to dryness on the water-bath. The remaining *d*-*iso*menthylamine *d*-tartrate separated from boiling water in large glistening plates, m. p. 204°, $[\alpha]_D$ + 32·9°, $[M]_D$ + 151°.

Upon replacing the *d*-base by the *dl*-base in the above experiment and crystallising the product from acetone–methyl alcohol, three successive fractions were obtained with $[M]_D$ + 108°, + 56°, and + 55°, respectively. The rotatory power of the first fraction remained practically unaltered upon recrystallisation, even when the sterile solution was seeded with a crystal of pure *d*-*iso*menthylamine *d*-tartrate; when decomposed, it yielded optically impure *d*-*iso*menthylamine hydrochloride with $[M]_D$ + 15°. A fraction of the original salt with $[M]_D$ + 51° yielded optically inactive *iso*menthylamine hydrochloride.

4. *Hydrogen Tartrates*.—*d*-*iso*Menthylamine hydrogen *d*-tartrate, prepared from the free acid and base, crystallised from acetone–methyl alcohol in fine needles, m. p. 190°, $[M]_D$ + 98°.

When mixed in equimolecular proportion in hot aqueous solution, *dl*-*iso*menthylamine and *d*-tartaric acid yielded a crystalline salt having $[M]_D$ + 45°, and this value remained practically unaltered upon fractionating the salt from the same solvent, even when the saturated solution was seeded with pure *d*-*iso*menthylamine hydrogen *d*-tartrate. Specimens of *iso*menthylamine hydrochloride prepared from these fractions were invariably optically inactive. As the molecular rotatory power in dilute aqueous solution of the hydrogen *d*-tartrate ion is about + 42°, it would appear that these separations all consisted of *dl*-*iso*menthylamine hydrogen *d*-tartrate; whether

this salt forms a partial racemate, or merely a conglomerate whose components cannot be separated owing to their similar solubilities, remains undecided.

Effect of Evaporation on the Rotatory Powers of Menthylamine Salts in Aqueous Solution.

1. A specimen of *l*-menthylamine hydrochloride having $[\alpha]_D$ $-35{\cdot}3°$ (0·5040 g. in 20 c.c. of water gave α_D $-1{\cdot}78°$) showed no alteration in rotatory power after evaporation to dryness in aqueous solution. The base was liberated with sodium hydroxide, extracted with ether, and reconverted into hydrochloride; the crude dry salt had $[\alpha]_D$ $-35{\cdot}2°$ in aqueous solntion (0·6114 g. in 25 c.c. gave α_D $-1{\cdot}72°$).

2. *Salts with* d-*α-Bromocamphor-π-sulphonic Acid.*—A specimen of the salt with *d-neo*menthylamine having $[M]_D$ $+341°$ (0·1160 g. in 20 c.c. gave α_D $+0{\cdot}85°$, $[\alpha]_D$ $+73{\cdot}3°$) was dissolved in water and evaporated to dryness on the water-bath; the dry recovered salt had $[M]_D$ $+310°$ (0·1082 g. in 20 c.c. gave α_D $+0{\cdot}72°$, $[\alpha]_D$ $+66{\cdot}5°$). The corresponding values for a specimen of the salt with *dl-neo*menthylamine were $[M]_D$ $+301°$ originally (0·1104 g. in 25 c.c. gave α_D $+0{\cdot}57°$, $[\alpha]_D$ $+64{\cdot}5°$), and $[M]_D$ $+264°$ after evaporation (0·1184 g. in 20 c.c. gave α_D $+0{\cdot}67°$, $[\alpha]_D$ $+56{\cdot}6°$). In a similar experiment the value of $[M]_D$ rose from $+282°$ to $+334°$ after evaporation in the presence of a small quantity of ammonia.

3. *Salts with* d-*Camphor*-10-*sulphonic Acid.*—The differences in rotatory power observed on applying similar treatment to salts of this acid with *d-neo-* and *dl-neo*-menthylamine were so slight as to be indistinguishable from possible experimental errors in making the polarimetric observations.

4. *Salts with* d-*Tartaric Acid.*—The normal *d*-tartrate of *d-neo*menthylamine and the normal and hydrogen *d*-tartrates of *dl-neo*menthylamine yielded results similar to those just indicated under (3).

In all these experiments the hydrochloride of the base was prepared from the original salt and from the specimen remaining after evaporation; in no instance, however, was any appreciable difference in rotatory power observed between the two specimens of the hydrochloride.

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United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, October 27th, 1928.*]

VI.—*Tertiary Phosphines containing the* n-*Butyl Radical.*

By Walter Cule Davies and William Jacob Jones.

No such phosphines have hitherto been described, but in the course of an investigation now being carried out by the authors on the action of the chlorides of phosphorus on the organo-magnesium halides, the following have been prepared : *tri*-n-*butylphosphine*, *phenyldi*-n-*butylphosphine* and p-*tolyldi*-n-*butylphosphine*. Triethylphosphine (Hibbert, *Ber.*, 1906, **39**, 161), triphenylphosphine (Pfeiffer, *Ber.*, 1904, **37**, 4620), phenyldimethylphosphine (Meisenheimer, *Annalen*, 1926, **449**, 227; Ingold, Shaw, and Wilson, J., 1928, 1280), and phenyldiethylphosphine (Meisenheimer, *loc. cit.*) have already been prepared by this method.

Preparation of the Phosphines.—A solution of 42 c.c. of *n*-butyl bromide in 100 c.c. of absolute ether, together with a granule of iodine, was added in the course of 3 hours to 10 g. of magnesium turnings and 150 c.c. of ether, contained in an apparatus through which hydrogen was passed throughout the course of the preparation, and which permitted of continuous stirring of the liquid. The resulting Grignard solution was cooled to 0° and a solution of 9 c.c. of phosphorus trichloride or 19 c.c. of phenyldichlorophosphine or 20 c.c. of *p*-tolyldichlorophosphine in 50 c.c. of ether was added drop by drop. The mixture was then warmed for ½ hour on the water-bath, cooled below 0°, and cautiously treated with a solution of 50 g. of ammonium chloride in 250 c.c. of water; the precipitated magnesium salts ultimately all dissolved. The ethereal solution was dried over anhydrous sodium sulphate, and the ether distilled off, in an atmosphere of carbon dioxide. The residue was fractionally distilled, and the phosphine redistilled, under 50 mm. pressure. All thermometer readings given are corrected.

The *n*-butylphosphines are colourless liquids having the characteristic phosphinic odour. They are miscible in all proportions with alcohol, ether, and benzene, but immiscible with water, and their molecular weights in freezing benzene are normal. They are far less easily oxidised than the lower tertiary phosphines. For instance, they do not readily combine with the oxygen of the air, but tri-*n*-butylphosphine, on being boiled in a current of air, is converted into *tri*-n-*butylphosphine oxide*. Tri-*n*-butylphosphine combines directly with carbon disulphide to give a deep red, crystalline *compound*, but from phenyl- and *p*-tolyl-di-*n*-butylphosphines, although deep red solutions are obtained in carbon disulphide, no

crystalline compounds can be produced. All these phosphines combine with alkyl iodides and with mercuric chloride. The phosphonium iodides are ionised in aqueous and in alcoholic solution, and can be quantitatively estimated by means of silver nitrate. *Vigorous reaction also occurs between the phosphines and both chlorine and sulphur.*

*Tri-*n*-butylphosphine* has b. p. 149·5°/50 mm. and $d_4^{25°}$ 0·8118 (Found: C, 70·8; H, 13·8; *M*, 210. $C_{12}H_{27}P$ requires C, 71·2; H, 13·5%; *M*, 202). Yield, 11 g. The *carbon disulphide addition compound*, $C_{12}H_{27}P,CS_2$, m. p. 65·5° (Found: C, 56·1; H, 10·1. $C_{13}H_{27}S_2P$ requires C, 56·1; H, 9·8%), owing to the vigour of the combination, is best prepared by mixing cold absolute-alcoholic solutions of the components, from which the compound crystallises. It is completely dissociated in hot ethereal and alcoholic solutions. On mixing alcoholic solutions of the components the mercuric chloride addition compound of tri-*n*-butylphosphine is obtained as a plastic mass which is difficult to purify. *Methyltri-*n*-butylphosphonium iodide*, owing to the violence of the direct interaction of methyl iodide and the phosphine, is most conveniently obtained by mixing dilute ethereal solutions of the reactants; the white crystalline precipitate, m. p. 133·5°, is purified by washing with ether (Found: I, 36·1. $C_{13}H_{30}IP$ requires I, 36·8%). *Ethyltri-*n*-butylphosphonium iodide* (Found: I, 34·9. $C_{14}H_{32}IP$ requires I, 35·4%) melts at 153°. *Tri-*n*-butylphosphine oxide* was prepared by adding 10 c.c. of phosphorus oxychloride in 50 c.c. of ether to the Grignard solution already described. Ammonium chloride solution was added and, when the ethereal layer was fractionally distilled under 760 mm. pressure, the oxide passed over at 300° and solidified in the receiver (Found: C, 63·3; H, 12·6; P, 14·9. $C_{12}H_{27}OP$ requires C, 66·0; H, 12·4; P, 14·2%). It forms colourless needles which are extremely hygroscopic. The oxide was also prepared both by boiling the phosphine in a current of air and by oxidising it with warm 40% nitric acid.

*Phenyldi-*n*-butylphosphine* has b. p. 184·5—185·5°/50 mm. and $d_4^{25°}$ 0·9115 (Found: C, 75·4; H, 10·5; P, 14·6; *M*, 221. $C_{14}H_{23}P$ requires C, 75·6; H, 10·4; P, 14·0%; *M*, 222). Yield, 16 g. The *mercuric chloride compound*, m. p. 160·5°, is obtained as fine needles when alcoholic solutions of its components are mixed and is purified by recrystallisation from alcohol (Found: Cl, 14·7. $C_{14}H_{23}P,HgCl_2$ requires Cl, 14·4%). *Phenylmethyldi-*n*-butylphosphonium iodide* is not so soluble in water as the other iodides, and well-formed rods, m. p. 168°, are obtained on recrystallisation from water (Found: I, 34·3. $C_{15}H_{26}IP$ requires I, 34·8%).

*Phenylethyldi-*n*-butylphosphonium iodide* melts at 147° (Found:

I, 33·9. $C_{16}H_{28}IP$ requires I, 33·6%). It is best recrystallised from alcohol–ether.

p-*Tolyldi*-n-*butylphosphine* has b. p. 197°/50 mm. and $d_4^{25°}$ 0·9076 (*Found : C*, 75·5; H, 10·8; *M*, 228. $C_{15}H_{25}P$ requires *C*, 76·1; H, 10·7%; *M*, 236). Yield, 15 g. The *mercuric chloride addition compound* crystallises from alcohol in prisms, m. p. 112° (Found : Cl, 14·2. $C_{15}H_{25}P,HgCl_2$ requires Cl, 14·0%). p-*Tolylmethyldi*-n-*butylphosphonium iodide* melts at 130·5° (Found : I, 33·5. $C_{16}H_{28}IP$ requires I, 33·6%).

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF. [*Received, November 21st*, 1928.]

VII.—*The Iodometric Estimation of Iron.*

By (the late) EGERTON CHARLES GREY.

THE volumetric determination of iron by titration with sodium thiosulphate of the iodine liberated through the interaction of a soluble iodide and a ferric salt, which was first suggested by Mohr (*Annalen*, 1858, **105**, 53), is based upon the reaction $2HI+2FeCl_3=2HCl+I_2+2FeCl_2$. This reaction is known to be reversible, and the blue colour of the starch may return in spite of repeated discharge by thiosulphate. No explanation has been offered of the phenomenon, but various recommendations have been made, such as exclusion of air by a current of carbon dioxide, heating the solution to 60°, waiting 20 minutes before titration, and using very little hydrochloric acid, all of which are based upon a misconception of the nature of the reaction.

To realise the proper conditions necessary for carrying out the accurate estimation of iron by the above method, the process must be considered in two parts : (1) the liberation of iodine from hydriodic acid by the action of the ferric salt, and (2) the titration of the iodine. The conditions for the two operations are not the same.

(1) The first operation is essentially a mutual discharge of ferric and iodide ions and should be represented thus: $2Fe^{\cdot\cdot\cdot} + 2I' = 2Fe^{\cdot\cdot} + I_2$. The reaction therefore should depend merely on the effective concentration of these two ions. In the presence of water, however, the effective concentration of ferric ions is reduced owing to hydrolysis and formation of ferric hydroxide; this follows instantly upon dilution, increases with the time, and is vastly accelerated by the addition of hydroxyl ions, which appear, for example, on the decomposition of potassium iodide in water.

Therefore, the greater the amount of water employed, and the greater the amount of potassium iodide, the larger must be the addition of hydrogen ions. Thus, for the liberation of iodine, there *must* be a large excess both of iodide and of acid.

The preparation of a solution of iron in which the metal is actually *in the soluble form and not colloidal* is essential, and if the solution is to be kept stable it must contain acid of not less than about *N* concentration.

If a clear solution possessing the bright lemon-yellow colour of the ferric salt or ferric ions is treated with an equal volume of concentrated hydrochloric acid and sufficient potassium iodide (about 5·5 mols. of iodide to each *atom of iron*), the *iodine* will *be liberated* practically instantaneously, and may be immediately titrated with a theoretical result. In order to avoid this large excess of acid, it suffices to use *N*-acid, the reaction being then complete, whatever the concentration of iron, in 3 minutes at room temperature. No reversion is to be observed in these circumstances, and titration may be made at any later time.

(2) If the iron was truly in the state of a dissolved ferric salt when the iodide was added, the solution may be freely diluted with water after 3 minutes, and titrated with starch as indicator. The end point should be sharp and there should be no return of blue colour. The reoxidation of ferrous iron by the air in these circumstances is negligible or non-existent, and precautions to avoid this are superfluous. The solution after titration by thiosulphate may be shaken violently with air for 2 hours without any return of the blue colour even when the acidity is that of *N*-hydrochloric acid, and however dilute the iodide, but if hydrogen peroxide be added in a concentration corresponding to that of oxygen in saturated water, the appearance of free iodine is almost instantaneous: the oxidation by atmospheric oxygen, if it occurs at all, is about one million times slower than by hydrogen peroxide in equivalent oxygen concentration.

The above statements are true for pure solutions, provided that the iron was present *as ferric ions when mixed with the iodide* but if not, the blue colour will return. In the presence of various impurities, hydrogen iodide will decompose at a rate proportional *to the concentration of its ionised portion.* This may be prevented either by raising the concentration of iodide ions or by lowering the concentration of hydrogen ions, as, *e.g.*, by the addition of sodium acetate. This addition is only necessary if impurities are present.

The factors which cause the return of the blue colour after thiosulphate titration by discharging iodide ions are: (1) colloids

ferric hydroxide or suspended oxide, which may be introduced with the reagents; (2) hydrogen acceptors (oxidising agents) such as chlorine or nitric acid; (3) copper. Oxidising agents present as impurities will give high results but will not cause a return of blue colour after titration unless they are added in the distilled water.

In the absence of colloidal ferric hydroxide (or oxide), therefore, the only cause of the returning blue colour is copper. In the analysis of the ash of plants and animals for iron, this metal will frequently be found, and may be recognised and even estimated with fair accuracy by the rate of return of the blue colour, other causes having been eliminated.

The effect is readily distinguishable from others in that it is catalytic; by means of the effect it is possible to distinguish 1—2 parts of copper in 2,000,000 parts of water. The presence of copper naturally leads to high results, and it must be removed if its effect is significant. With solutions of iron not weaker than $N/400$, this may be done readily by adding an excess of ammonium hydroxide, which leaves the copper entirely in solution.

The detailed procedure for successful use of the method is, therefore, as follows:

(*a*) Incinerate the material to remove organic matter, evaporate repeatedly with concentrated hydrochloric acid until any insoluble residue is colourless, and adjust the hydrochloric acid content of the final solution so that it is not less than 0·4 c.c. of concentrated acid in 10 c.c. (The total volume of acid employed should be noted, for a control may be necessary on the iron which it probably contains.) If the estimation is delayed, avoid diluting the acid ferric solution until immediately prior to the estimation, especially when the amount of iron is small.

(*b*) If copper is present, add excess of ammonium hydroxide, filter, wash, and redissolve the precipitate in acid.

(*c*) To 10 c.c. of the ferric chloride solution add 0·33 g. of potassium iodide dissolved in not more than 5 c.c. of water (= 2 c.c. of M-potassium iodide). The liberation of iodine is complete in 3 minutes at 15°.

(*d*) Dilute the above mixture with pure distilled water; add sodium acetate if desired, and titrate with thiosulphate of suitable strength. If very dilute thiosulphate is used, it must be freshly made each day. With $N/2000$-thiosulphate it is possible to estimate accurately quantities of the order of 0·05 mg. Fe.

The thiosulphate may be standardised on potassium dichromate, the procedure being the same as with the estimation of iron, except that hydrolysis does not interfere.

EXPERIMENTAL.

Numerous experiments have shown that 5·5 mols. of potassium iodide are required per atom of iron, and the concentration in the titrated liquid should be adjusted to about $M/7{\cdot}5$, and the acid concentration should be $N/3$—$3N$. In such a case the liberation of iodine will be strictly proportional to the iron present, within the limits 0·056—56 mg. of iron in 10—50 c.c. of liquid.

Any reagent causing lowering of hydrogen-ion concentration, *e.g.*, sodium acetate, thus favouring hydrolysis of ferric chloride, tends to produce recurrence of the blue colour. Old solutions of iron salts contain iron hydroxide, which dissolves slowly, and therefore they cause a slow recurrence of the blue colour. On the other hand, freshly made ferric chloride solutions, on dilution with water, contain hydroxide in a form which dissolves rapidly. Hence, in this case, the blue colour reappears rapidly and the total liberation of iodine comes to an end more quickly. This cause of the recurring blue colour is therefore quite distinct from the catalytic action of copper.

It will be noted that low hydrogen-ion concentration favours the recurrence of the colour due to the presence of ferric hydroxide, but also increases the stability of hydriodic acid in the presence of impurities.

The effect of copper is shown by the following results:

($N/40$-$FeCl_3$ containing 0·4% HCl: $M/7$-KI solution.)

1. 10 c.c. Fe soln. + 2 c.c. KI + 3 c.c. water after 5 mins. = 10·16 c.c. $N/40$ $Na_2S_2O_3$.
2. 10 c.c. Fe soln. + 4 c.c. KI + 1 c.c. water after 5 mins. = 10·32 c.c. $N/40$ $Na_2S_2O_3$.
3. 10 c.c. Fe soln. + 2 c.c. KI + 3 c.c. $M/200$-$CuSO_4$ (= 0·96 mg. Cu) = 10·[illegible] c.c. $N/40$-$Na_2S_2O_3$.

Less than 2 c.c. of $M/200$-copper sulphate does not immediately affect the liberation of iodine with this quantity of iron, but produces later the characteristic catalytic effect. No. 2 remained colourless for many hours, and No. 1 became coloured in 15 minutes owing to insufficient potassium iodide; No. 3 coloured rapidly and in 12 minutes required an extra 0·43 c.c. of $N/200$-thiosulphate.

The power to cause recurrence of colour is possessed only by metallic ions which can change from higher to a lower valency, such as $Fe^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Mn^{\cdot\cdot\cdot\cdot}$; all other basic ions tried, including $Na^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, were quite without influence upon the velocity of decomposition of hydrogen iodide, even when present in considerably more than equivalent concentration.

The catalytic activity of the cupric ion in discharging iodide ions is illustrated in the following table, which shows the amount of iodine liberated in one hour.

Copper added, mg.	Iodine liberated (c.c. of $N/2000$).	Mg. of Cu per c.c. $N/2000$-iodine (calc. 0·0032).
0·05	10·8	0·004
0·025	6·3	0·004
0·0125	4·2	0·003
0·0063	2·7	0·003
0·0031	1·96	0·002
0·0016	0·86	0·002

Small quantities of copper thus produce a marked catalytic effect. This gives a method of distinguishing 1—2 parts of Cu in 1,000,000 parts of water.

My best thanks are due to Sir F. Gowland Hopkins, F.R.S., in whose laboratory the work was done.

THE SIR WILLIAM DUNN INSTITUTE OF BIOCHEMISTRY,
THE UNIVERSITY, CAMBRIDGE. [*Received, July 21st*, 1928.]

VIII.—N-*Substituted Derivatives of Piperazine and Ethylenediamine. Part I. The Preparation of* N-*Monosubstituted Derivatives.*

By TOM SIDNEY MOORE, MARY BOYLE, and VERA M. THORN.

WHEN piperazine reacts with substances capable of attacking its imino-groups, the products are almost invariably the *N*-disubstituted derivatives. For instance, dibenzoyl-, ditoluenesulphonyl-, and dicarbethoxy-piperazine are the sole products even when the reactions with the corresponding halogen compounds are carried out with an excess of piperazine. With alkyl iodides the dialkyl compounds and the quaternary derivatives $R\cdot N<C_4H_8>NR_2I$ and $IR_2N<C_4H_8>NR_2I$ only can be isolated (Hofmann, *Compt. rend.*, 1859, **49**, 788; van Ryl, *Dissert.*, Zürich, 1897; Strömholm, *Ber.*, 1903, **36**, 143).

Various *N*-monosubstituted derivatives being required for other work, attempts were made to find reaction conditions which would allow of their isolation, but only in one case—that of *piperazinoacetic acid*, $HN<C_4H_8>N\cdot CH_2\cdot CO_2H$—was a direct method successful. If ethyl chloroacetate (2 mols.) reacts with piperazine (3 mols.) in dry alcoholic solution, the esters of piperazinoacetic acid and of piperazinediacetic acid, $C_4H_8(N\cdot CH_2\cdot CO_2H)_2$, are both formed, together with piperazine hydrochloride. By removal of the last and hydrolysis of the esters a mixture of the hydrochlorides of the acids is obtained, and a separation is possible since the hydrochloride of the dibasic acid is practically insoluble in water; but the process is tedious and the yield small (about 30% yield of the monobasic acid). Attempts to prepare β-piperazinopropionic

acid, $HN<C_4H_8>N\cdot[CH_2]_2\cdot CO_2H$, and γ-piperazinobutyric acid, $HN<C_4H_8>N\cdot[CH_2]_3\cdot CO_2H$, by similar methods failed, for, although in each case the mixture of mono- and di-basic acids was obtained, no method of separation giving pure products could be found.

Attempts were therefore made to find conditions for the preparation of the unknown monoacyl derivatives of piperazine, since a substance of the type $HN<C_4H_8>N\cdot COR$ should allow of the preparation of the compounds $R_1N<C_4H_8>N\cdot COR$ which on hydrolysis would give $R_1N<C_4H_8>NH$, where R_1 is any desired substituent.

Since ethyl chloroformate even with excess of piperazine produces only the dicarbethoxy-compound, it is evident that the rate of reaction of the chloroformic ester with *monocarbethoxypiperazine*, which, presumably, is the first product, is specifically very much *greater than* the *rate of reaction* of the ester with piperazine; for otherwise some monocarbethoxypiperazine must remain in the solution. And the same must be true of the relative rates of reaction with piperazine and with the monosubstituted piperazine of all the compounds which produce only disubstituted derivatives. This relation seemed so remarkable that later, when the mono-substituted derivatives had been prepared and their properties were known, special experiments were made to find out whether, in fact, mono-substituted derivatives were formed under ordinary conditions, but had escaped isolation; no such derivatives could be detected.

The following considerations show that the possibility of survival of a monosubstituted derivative is much increased if the reaction is carried out in acid solution. A salt of a diacid base, such as piperazine, undergoes hydrolysis in aqueous solution in two stages represented by the equations (anions omitted)

$$H_2\dot{N}<C_4H_8>\dot{N}H_2 + H_2O \rightleftharpoons H_2\dot{N}<C_4H_8>NH_2\cdot OH + \dot{H} \rightleftharpoons H_2\dot{N}<C_4H_8>NH + \dot{H} + H_2O \quad . \quad . \quad . \quad . \quad (1)$$

$$\underset{y}{H_2\dot{N}<C_4H_8>NH} + H_2O \rightleftharpoons \underset{x_1}{HO\cdot H_2N<C_4H_8>NH} + \dot{H} \rightleftharpoons \underset{x_2}{HN<C_4H_8>NH} + \dot{H} + H_2O \quad . \quad . \quad . \quad . \quad (2)$$

These equations represent respectively the hydrolysis corresponding to the second and the first dissociation constant of the base itself; and since the second dissociation constant of a diacid base must be much smaller than the first—just as in dibasic acids—the degree of hydrolysis corresponding to equation (1) will be much greater than that corresponding to equation (2). We have not the data necessary for finding the separate values of x_1 and x_2 in equation

(2); but putting $x = x_1 + x_2$, we find that y/x is given by the expression [H] . K_b/K_w, where [H] is the concentration of hydrion, K_b is the "apparent" first dissociation constant of piperazine, and K_w is the ionic product of water. Using the known values of K_b and K_w (Landolt–Börnstein, "Tabellen," 1923), the value of y/x is found to be [H] $\times 10^{10}$ and is thus very large even in weakly acid solution.

If a reactive halogen compound, *e.g.*, ethyl chloroformate, is added to a solution of piperazine hydrochloride, it can react with $H_2\dot{N}<C_4H_8>NH$ to form $H_2\dot{N}<C_4H_8>N{\cdot}CO_2Et$, the kation of the salt of the monocarbethoxy-compound. Comparatively very little reaction can occur with $HN<C_4H_8>NH$, since its concentration is relatively small. But the salt of the monocarbethoxy-compound will itself undergo hydrolysis according to the equation

$$\underset{m}{H_2\dot{N}<C_4H_8>N{\cdot}CO_2Et} + H_2O \rightleftharpoons \underset{l_1}{HO{\cdot}H_2N<C_4H_8>N{\cdot}CO_2Et} + \dot{H}$$

$$\rightleftharpoons \underset{l_2}{HN<C_4H_8>N{\cdot}CO_2Et} + H_2O + \dot{H} \quad . \quad . \quad . \quad (3)$$

The extent of this hydrolysis depends on the dissociation constant of the monocarbethoxy-compound, which will probably be smaller than, but at any rate of an order of magnitude not very different from, the first dissociation constant of piperazine, so that the ratio m/l, where $l = l_1 + l_2$ in equation (3), will be of much the same order as the ratio y/x, *i.e.*, very large. Thus, of the four substances in the solution containing iminic hydrogen, which are therefore capable of reacting with ethyl chloroformate, *viz.*, $H_2\dot{N}<C_4H_8>NH$, $HO{\cdot}H_2N<C_4H_8>NH$, $HN<C_4H_8>NH$, and $HN<C_4H_8>N{\cdot}CO_2Et$, the first has a concentration very large compared with the concentrations of the other three, so long as the solution is acid. When half the piperazine has reacted, and if the solution is $N/1000$ with regard to hydrion, the concentration of $H_2\dot{N}<C_4H_8>NH$ is probably more than a million times the concentration of $HN<C_4H_8>N{\cdot}CO_2Et$. So that even though the specific rate of reaction of ethyl chloroformate with monocarbethoxypiperazine is so much greater than its rate of reaction with piperazine, the ratio of the concentration of $HN<C_4H_8>N{\cdot}CO_2Et$ to that of $H_2\dot{N}<C_4H_8>NH$ in acid solution is so small, and therefore so unfavourable to the former reaction, that a considerable quantity of monocarbethoxypiperazine should remain in the solution as hydrochloride.

Although concentration ratios become more favourable for the purpose in view the higher the hydrion concentration is maintained during the reaction, there must be an upper limit to the useful concentration of hydrion, since the concentrations of both

$H_2\dot{N}{<}C_4H_8{>}NH$ and $HN{<}C_4H_8{>}N{\cdot}CO_2Et$ diminish with increasing hydrion concentration, and a point must be reached when the rate of reaction would become inconveniently small. Other things being equal, the halogen compound which has the greatest rate of reaction with piperazine should therefore give the best results in practice, since for a given duration of the experiment it will allow of the highest hydrion concentration.

Preliminary experiments showed that of ethyl chloroformate, benzoyl chloride, and toluenesulphonyl chloride, the first reacts most quickly with piperazine; and that the rate of reaction of the ester with piperazine becomes too small for preparative purposes if the acidity exceeds approximately 0·0015*N* ($p_H = 2{\cdot}8$). The procedure found successful was the following. To a concentrated solution of piperazine containing some bromophenol-blue (p_H 2·8—4·6), 2*N*-hydrochloric acid was added until the neutral tint of the indicator appeared. Small quantities of ethyl chloroformate and 2*N*-sodium hydroxide were run in at intervals, with vigorous stirring, each addition of ester being allowed to disappear before the addition of the alkali, and only sufficient of the latter being added at one time to bring the colour of the indicator back to the neutral tint. The process was continued until a test showed that no piperazine remained. The solution so obtained contains both mono- and di-carbethoxypiperazines, of which the latter is readily extracted by ether after addition of excess of alkali, whereas the *monocarbethoxypiperazine* is hardly extracted at all until the solution has been saturated with potassium carbonate. The yields of the mono- and the di-derivative correspond to 70% and 12%, respectively, of the piperazine used. The proportion of mono- to dicarbethoxypiperazine falls either if a less acid indicator is used, or if the additions of alkali are made before the previous addition of ethyl chloroformate has been used up—no doubt on account of the momentary alkalinity where the drops of alkali enter the solution.

In later experiments the necessary degree of acidity was maintained by addition of a strong solution of sodium acetate, instead of sodium hydroxide. On account of the buffering action of the sodium acetate–acetic acid mixture, the concentration of hydrion rises only slowly as hydrochloric acid is liberated during the reaction, so that it is kept nearer the most favourable point. The yields were practically unaltered, but the duration of the experiment was reduced from about 4½ hours to about 2½ hours, and less ethyl chloroformate, of which a considerable amount is lost by evaporation and hydrolysis, was required.

With benzoyl chloride under similar conditions the yield of *monobenzoylpiperazine* was only 22% of the theoretical; with toluene-

sulphonyl chloride the reaction was exceedingly slow, and no monotoluenesulphonyl compound could be isolated.

Since the method should apply in general to diacid bases, experiments were carried out with ethylenediamine, another base of which no *N*-mono-alkyl or -acyl derivatives have yet been described. The most favourable hydrion concentration for the reaction with ethyl chloroformate in this case is approximately 0·0001*N* ($p_H = 4$), corresponding to the acidic end of the range covered by bromocresol-green. With sodium hydroxide the experiment takes 7 hours, and with sodium acetate 3½ hours, but the yields are slightly better with the former and are 60—70% of the theoretical yield of *monocarbethoxyethylenediamine*, $H_2N{\cdot}C_2H_4{\cdot}NH{\cdot}CO_2Et$, and 10% of the dicarbethoxy-compound.

The preparation of compounds $RN{<}C_4H_8{>}N{\cdot}CO_2Et$ from carbethoxypiperazine offered little difficulty. The carbethoxy-group is removed from these compounds rapidly (2 hours) by boiling alkali, but only very slowly (2—3 days) by boiling hydrochloric acid. Nevertheless the latter method is in many cases more convenient, for several of the products are best isolated as hydrochlorides. If R is an acidic radical, it is usually removed with the carbethoxy-group, so that, except for the toluenesulphonyl derivative, the monoacyl compounds cannot be prepared through the carbethoxy-compounds. But it should be possible to prepare such derivatives directly, in acid solution, and this has been done in the case of monobenzoylpiperazine.

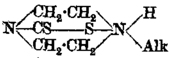
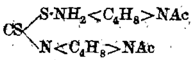
The solubilities of the compounds $RN{<}C_4H_8{>}N{\cdot}CO_2Et$ are somewhat remarkable. When R is benzoyl or toluenesulphonyl, the compounds are readily soluble in the common organic solvents, but are practically insoluble in water; when R is C_2H_5, $C_2H_4{\cdot}OH$, $CH_2{\cdot}CO_2Et$ or $[CH_2]_2{\cdot}CO_2Et$, the compounds are liquids miscible in all proportions with water, as well as with organic solvents (benzene, ether, chloroform) at the ordinary temperature, but the aqueous solution of *carbethoxyethylpiperazine* separates into two phases on warming.

Of the compounds $HN{<}C_4H_8{>}NR$ which have been prepared, all except *toluenesulphonylpiperazine* are exceedingly soluble in water. Thus carbethoxy- and *ethyl-piperazine* are practically not extracted from aqueous solution by ether, with which, however, they are both completely miscible; benzoylpiperazine is not extracted from aqueous solution by ether, in which it is very soluble; and all three compounds mix with or dissolve in benzene. On the other hand, the acids $HN{<}C_4H_8{>}N{\cdot}[CH_2]_n{\cdot}CO_2H$ (where $n = 1$, 2, or 3) are practically insoluble in organic liquids except that they are sparingly soluble in hot alcohol—no doubt because they exist as internal salts

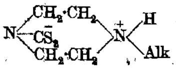
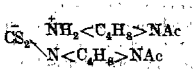
$HN<C_4H_8>\overset{+}{N}H\cdot[CH_2]_n\cdot\overset{-}{C}O_2$ or $H_2\overset{+}{N}<C_4H_8>N\cdot[CH_2]_n\cdot\overset{-}{C}O_2$. From aqueous solution piperazinoacetic acid crystallises, or is precipitated by alcohol, as hydrated crystals, which retain one molecule of water per molecule even over sulphuric acid and dehydrate exceedingly slowly over phosphoric oxide; the other two acids cannot be made to crystallise from water and are precipitated by alcohol in anhydrous forms. Piperazinoacetic acid thus resembles piperidinoacetic acid, which retains one molecule of water with great tenacity (Bischoff, *Ber.*, 1898, **31**, 2841; Wedekind, *Ber.*, 1899, **32**, 723), rather than glycine, which is anhydrous. But if the combination with water is to be attributed to the grouping common to these two acids, $R<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>\overset{+}{N}H\cdot CH_2\cdot\overset{-}{C}O_2$, where R is NH in piperazinoacetic acid and CH_2 in piperidinoacetic acid, it is difficult to see why the two higher acids do not share this property.

The salts of these acids are in some cases complex. For instance, the very dark blue copper salt of piperazinoacetic acid gives on dehydration a green salt which does not revert to the blue under any conditions tried, and in both the blue and the green solution some of the normal reactions for copper are absent. A detailed investigation of these salts is being undertaken.

The monosubstituted piperazines form with carbon dioxide unstable, and with carbon disulphide stable, *addition compounds*, of which the latter are formed with considerable heat evolution, sublime almost without decomposition, and are not desulphurised by metallic oxides. The molecular proportion of carbon disulphide to base in these compounds is 1 : 1 with ethylpiperazine, as it is in the case of piperazine itself (Herz, *Ber.*, 1897, **30**, 1585), and 1 : 2 with monoacylpiperazines. Two basic groups, one containing a mobile hydrogen atom, thus appear to be necessary for the formation of these compounds, and in view of the similarity of their behaviour to that of the dithiocarbamates formed from secondary amines (Grodzki, *Ber.*, 1881, **14**, 2756) they may be formulated as

 and 

or more probably,

 and 

A few compounds $R\cdot NH\cdot C_2H_4\cdot NH\cdot CO_2Et$ and $R\cdot NH\cdot C_2H_4\cdot NH_2$ were prepared from carbethoxyethylenediamine by the same methods as were used for the piperazine derivatives, which they resembled in

general properties. Lower yields and the occurrence of residues during purification indicated that side reactions took place, as indeed would be expected since both ring-formation and condensation are obviously possible with most of the substances involved. The acid $H_2N{\cdot}C_2H_4{\cdot}NH{\cdot}CO_2H$ (which was prepared so that its salts might be compared with those of the acids derived from piperazine) is readily obtained anhydrous, differing thus from piperazinoacetic acid.

EXPERIMENTAL.

Derivatives of Piperazine.

Ethyl Piperazine-1-carboxylate (*N-Carbethoxypiperazine*), $HN{<}C_4H_8{>}N{\cdot}CO_2Et$.
—Ethyl chloroformate (25—32 c.c.) was allowed to react with piperazine (38·8 g. of hexahydrate) under the conditions described on p. 42, the additions of ester and sodium acetate being continued until the product of benzoylation of a few drops of the solution was completely soluble in ether. (Benzoylcarbethoxypiperazine is soluble, and dibenzoylpiperazine, which is formed on benzoylation so long as the solution still contains piperazine, is insoluble in ether. If unchanged piperazine remains, some of it will be extracted with the carbethoxy-compound and complicate the purification of the latter.) Sodium hydroxide (100 c.c. of 20% solution) was added, with ice-cooling to diminish saponification of the esters, and the dicarbethoxypiperazine extracted with ether (3 extractions). The solution was then saturated with potassium carbonate (ice-cooling), filtered from precipitated salts, and extracted exhaustively with ether. From the ethereal solution, dried over sodium sulphate, a colourless viscid liquid, b. p. 116—117°/12 mm. and 237°/760 mm., was obtained. The yield (average) was 22·2 g., and also 5·7 g. of dicarbethoxypiperazine (Found: C, 53·3; H, 9·0. $C_7H_{14}O_2N_2$ requires C, 53·2; H, 8·9%). The substance mixes in all proportions with water and the common organic solvents. When carbon dioxide is passed through its dry ethereal solution, it forms an addition product which deliquesces in air and loses carbon dioxide in a desiccator. An *addition compound*, $2HN{<}C_4H_8{>}N{\cdot}CO_2Et,CS_2$, precipitated with evolution of heat when carbon disulphide is added to an alcoholic solution of the substance, is a faintly yellow powder, insoluble in water, sparingly soluble in alcohol and benzene, which sublimes rapidly at 130—140° and melts (decomp.) at 148° (Found: N, 14·2. $C_{15}H_{28}O_4N_4S_2$ requires N, 14·3%).

Ethyl 4-benzoylpiperazine-1-carboxylate, $C_6H_5{\cdot}CO{\cdot}N{<}C_4H_8{>}N{\cdot}CO_2Et$,
prepared by benzoylating carbethoxypiperazine in the cold in

presence of dilute alkali (*N*/10), is easily soluble in ether and benzene and is best recrystallised from light petroleum; m. p. 82° (Found: C, 64·4; H, 6·8. $C_{14}H_{18}O_3N_2$ requires C, 64·1; H, 6·9%).

N-*Benzoylpiperazine* can be obtained only in very small yield by shaking the preceding compound with cold *N*/10-sodium hydroxide, the main products being sodium benzoate and piperazine. It was prepared by direct benzoylation of piperazine under the conditions used in the preparation of carbethoxypiperazine (p. 42). At the end of the reaction the precipitate of dibenzoylpiperazine and benzoic acid was filtered off, the solution made alkaline, and the monobenzoylpiperazine extracted with chloroform. The substance is excessively hygroscopic, very soluble in the common organic solvents, but can be crystallised by evaporation of a dry ethereal solution in a desiccator; m. p. 64° (Found: C, 69·6; H, 7·6. $C_{11}H_{14}ON_2$ requires C, 69·5; H, 7·4%).

Ethyl 4-p-*toluenesulphonylpiperazine*-1-*carboxylate*,

$$C_7H_7\cdot SO_2\cdot N{<}C_4H_8{>}N\cdot CO_2Et,$$

was prepared by stirring an ethereal solution of *p*-toluenesulphonyl chloride with a weakly alkaline solution of carbethoxypiperazine. After recrystallisation from benzene and ligroin it melted at 121° (Found: C, 53·9; H, 6·3. $C_{14}H_{20}O_4N_2S$ requires C, 53·9; H, 6·4%).

N-p-*Toluenesulphonylpiperazine* was obtained by boiling the preceding compound with 10% alcoholic potassium hydroxide for 2 hours. It is sparingly soluble in water (alkaline solution) and easily soluble in benzene. After recrystallisation from benzene and ligroin it melts, slowly heated, at 110°, but when heated rapidly it melts at 102°, resolidifies, and melts again at 110° (Found: C, 55·2; H, 6·6. $C_{11}H_{16}O_2N_2S$ requires C, 55·0; H, 6·7%). An *addition compound*, $2C_{11}H_{16}O_2N_2S,CO_2$, was precipitated when carbon dioxide was passed through its alcoholic solution. This decomposes on boiling with water and melts at 107° (decomp.) (Found: S, 12·1. $C_{23}H_{32}O_6N_4S_2$ requires S, 12·2%). On addition of carbon disulphide to an alcoholic solution of toluenesulphonylpiperazine a faintly yellow *addition product*, $2C_{11}H_{16}O_2N_2S,CS_2$, was precipitated. It is insoluble in water and the common solvents, melts at 171°, but sublimes at lower temperatures with very slight decomposition (Found: S, 23·5. $C_{23}H_{32}O_4N_4S_4$ requires S, 23·0%).

Ethyl 4-*Ethylpiperazine*-1-*carboxylate*, $EtO_2C\cdot N{<}C_4H_8{>}NEt$.—When ethyl iodide reacts with carbethoxypiperazine in alcoholic solution a quaternary iodide is formed in addition to carbethoxyethylpiperazine, and it was not found possible to separate the latter compound from the carbethoxypiperazine left unchanged. A good yield (70—75%) of the *ethyl* derivative was obtained by heating

a solution of carbethoxypiperazine (12 g.) and excess of ethyl *p*-toluenesulphonate (20 g.) in dry alcohol (50 c.c.) with sodium carbonate (5·2 g.) at 100° until the evolution of carbon dioxide had ceased. After removal of the alcohol the residue was dissolved in 100 c.c. of *N*-sodium hydroxide and extracted with ether, a colourless viscid liquid, b. p. 136°/28 mm., being finally obtained (Found : C, 57·9; H, 9·7. $C_9H_{18}O_2N_2$ requires C, 58·1; H, 9·7%). The substance, which smells rather like triethylamine, mixes with water in all proportions at laboratory temperature, giving alkaline solutions which separate into two phases on warming.

N-*Ethylpiperazine dihydrochloride* was obtained as colourless, very deliquescent crystals by boiling the preceding compound with concentrated hydrochloric acid for 3 days, evaporating the solution, and precipitating the salt with alcohol (Found : Cl, 38·1. $C_6H_{14}N_2$,2HCl requires Cl, 37·9%).

N-*Ethylpiperazine.*—By heating the hydrochloride with dry slaked lime, drying the distillate with solid potash and redistilling it, *ethylpiperazine* was prepared as a colourless mobile liquid, b. p. 155—158° (Found : C, 62·7; H, 12·3. $C_6H_{14}N_2$ requires C, 63·2; H, 12·3%). The base, which smells like triethylamine, mixes with water, ether, and chloroform in all proportions and is extracted only with difficulty from its aqueous solutions. It forms a normal *chloroplatinate* (Found : Pt, 37·1. $C_6H_{14}N_2.H_2PtCl_6$ requires Pt, 37·2%) and *chloroaurate* (Found : Au, 49·2. $C_6H_{14}N_2$,2HAuCl$_4$ requires Au, 49·6%). An *addition compound*, $C_6H_{14}N_2$,CS_2, is formed with heat evolution as a yellow precipitate when carbon disulphide is added to an alcoholic solution of the base. It is insoluble in the common solvents, and sublimes very rapidly above 160° (Found : N, 14·8. $C_7H_{14}N_2S_2$ requires N, 14·7%).

Ethyl 4-β-*hydroxyethylpiperazine*-1-*carboxylate*,

$$EtO_2C{\cdot}N{<}C_4H_8{>}N{\cdot}C_2H_4{\cdot}OH,$$

was prepared by heating carbethoxypiperazine (30 g.) with excess of ethylene chlorohydrin (20 g.) and anhydrous sodium carbonate (13·5 g.) at 110° under reflux for 6 hours, by which time the evolution of carbon dioxide had ceased. The temperature was raised to 140° for 1 hour, and the mixture then made alkaline with 10% sodium hydroxide solution and extracted with ether. From the ethereal solution, dried over sodium sulphate, a viscid colourless liquid, b. p. 184°/17 mm., was obtained. Yield, 70% (Found : C, 53·2; H, 8·9. $C_9H_{18}O_3N_2$ requires C, 53·5; H, 8·9%). The substance mixes in all proportions with water and the common solvents.

N-β-*Hydroxyethylpiperazine dihydrochloride* was prepared by hydrolysing the preceding compound with concentrated hydrochloric acid for 2 days, evaporating the solution, and precipitating

the salt with alcohol (Found: Cl, 34·9. $C_6H_{14}ON_2,2HCl$ requires Cl, 34·9%). It forms a normal *chloroplatinate* (Found: Pt, 36·5. $C_6H_{14}ON_2,H_2PtCl_6$ requires Pt, 36·5%) and *chloroaurate* (Found: Au. 48·6. $C_6H_{14}ON_2,2HAuCl_4$ requires Au, 48·7%).

Ethyl 4-Carbethoxypiperazinoacetate,

$$EtO_2C{\cdot}N{<}C_4H_8{>}N{\cdot}CH_2{\cdot}CO_2Et.$$

—Equivalent weights of carbethoxypiperazine (15·8 g.), ethyl chloroacetate (12·3 g.), and anhydrous sodium carbonate (5·4 g.) were heated together on the steam-bath until the evolution of carbon dioxide ceased (1—1½ hours). After the mixture had cooled, water just sufficient to dissolve the whole mass was added, and the solution extracted with ether. From the ethereal solution a viscid liquid, b. p. 183°/18 mm., was obtained (Found: C, 53·8; H, 8·3. $C_{11}H_{20}O_4N_2$ requires C, 54·1; H, 8·2%). The substance mixes in all proportions with water (alkaline reaction) and the common solvents, except ligroin. Complete hydrolysis with acid requires 2—3 days, but after a few hours' heating, evaporation and treatment with potassium carbonate gives an alcohol-soluble potassium salt; this is probably $KO_2C{\cdot}CH_2{\cdot}N{<}C_4H_8{>}N{\cdot}CO_2Et$, since in other compounds the carbethoxy-group is very resistant to acids. Hydrolysis by alkalis is rapid, but, on account of the difficulty in recovering piperazinoacetic acid from its metallic salts, not convenient in practice.

Piperazinoacetic acid hydrochloride,

$$HN{<}C_4H_8{>}N{\cdot}CH_2{\cdot}CO_2H,2HCl,$$

is very soluble in water, but the aqueous solution gives anhydrous crystals which with slow crystallisation may be ¼ inch long or more (Found: Cl, 32·6. $C_6H_{12}O_2N_2,2HCl$ requires Cl, 32·7%). The crystals were kindly examined by Dr. T. V. Barker, who reports that they belong to the orthorhombic system with the following forms about equally developed: *a* (100), *b* (010), *c* (001), *q* (011), *o* (111) and *x* (221). The axial ratios, $a:b:c = 0{\cdot}9562:1:0{\cdot}6408$, were computed from the following two-circle measurements:

	a (100).	*b* (010).	*x* (221).	*o* (111).	*q* (011).	*c* (001).
ϕ	polar	0° 0′	37° 52′	*57° 21′	57° 21′	90° 0′
ρ	face	90 0	50 24	*60 34	90 0	90 0

Piperazinoacetic acid, $HN{<}C_4H_8{>}N{\cdot}CH_2{\cdot}CO_2H$ or

$$HN{<}C_4H_8{>}\overset{+}{N}H{\cdot}CH_2{\cdot}C\overset{-}{O_2},$$

was prepared by adding a suspension of silver carbonate to a boiling dilute solution of the hydrochloride, filtering the liquid hot, and removing the dissolved silver by means of hydrogen sulphide. (The solution, before treatment with the gas, is brown, and on standing deposits a few dark brown crystals of an explosive silver salt.) The acid was finally precipitated by alcohol from the concentrated

aqueous solution. It is very soluble in water (alkaline reaction), sparingly soluble in hot alcohol, and practically insoluble otherwise. From concentrated aqueous solutions it separates as transparent prisms which effloresce almost at once in air to a white powder; this loses no weight over sulphuric acid but still contains water which it loses at 100° or, very slowly, over phosphoric oxide (Found: C, 44·7; H, 8·7; N, 17·3; loss at 100°, 11·0. $C_8H_{12}O_2N_2,H_2O$ requires C, 44·5; H, 8·7; N, 17·3; H_2O, 11·1%). At 140—150°, the acid begins to darken and no melting takes place below 300°; when rapidly heated, it melts at 279°, decomposing into water and a mixture of solid products.

The procedure described on p. 48 served also for the preparation of *ethyl* 4-*carbethoxypiperazino*-β-*propionate*,

$$EtO_2C{\cdot}N{<}C_4H_8{>}N{\cdot}[CH_2]_2{\cdot}CO_2Et,$$

b. p. 198°/22 mm. (Found: C, 55·8; H, 8·5. $C_{12}H_{22}O_4N_2$ requires C, 55·9; H, 8·6%), from ethyl β-iodopropionate, and of *ethyl* 4-*carbethoxypiperazino*-γ-*butyrate*, $EtO_2C{\cdot}N{<}C_4H_8{>}N{\cdot}[CH_2]_3{\cdot}CO_2Et$, b. p. 207°/21 mm. (Found: C, 57·1; H, 8·8. $C_{13}H_{24}O_4N_2$ requires C, 57·4; H, 8·9%), from ethyl γ-chlorobutyrate, except that a higher temperature was required in the latter case. The further treatment of these esters to produce the four following compounds was the same as for the similar derivatives of acetic acid.

Piperazino-β-*propionic acid dihydrochloride* is too soluble to be crystallised from water, but is precipitated as extremely deliquescent crystals by alcohol (Found: Cl, 30·8. $C_7H_{14}O_2N_2,2HCl$ requires Cl, 30·7%).

Piperazino-β-*propionic acid*, $HN{<}C_4H_8{>}N{\cdot}[CH_2]_2{\cdot}CO_2H$ or $HN{<}C_4H_8{>}\overset{+}{N}H{\cdot}[CH_2]_2{\cdot}C\overset{-}{O_2}$, cannot be crystallised from water. It has an alkaline reaction. When heated quickly, it melts at 215°, but at 200° decomposition with subsequent melting is rapid (Found: C, 52·9; H, 8·8. $C_7H_{14}O_2N_2$ requires C, 53·2; H, 8·9%).

Piperazino-γ-butyric acid hydrochloride was too deliquescent for convenient handling, so the *chloroplatinate* was prepared for analysis (Found: Pt, 33·4. $C_8H_{16}O_2N_2,H_2PtCl_6$ requires Pt, 33·5%).

Piperazino-γ-butyric acid, $HN{<}C_4H_8{>}N{\cdot}[CH_2]_3{\cdot}CO_2H$ or $HN{<}C_4H_8{>}\overset{+}{N}H{\cdot}[CH_2]_3{\cdot}C\overset{-}{O_2}$, resembles the preceding acid in its solubilities. It melts at 235° with rapid heating, but decomposes slowly at lower temperatures.

Derivatives of Ethylenediamine.

Carbethoxyethylenediamine, $EtO_2C{\cdot}NH{\cdot}C_2H_4{\cdot}NH_2$, was prepared by the method described for carbethoxypiperazine, except that bromocresol-green was used as indicator. The substance is extracted

only slowly by ether from its aqueous solutions even after saturation with potassium carbonate. The smaller yield when sodium acetate is used (p. 43) is due to incomplete saturation with potassium carbonate, for there is a slow separation of potassium acetate from the solution during extraction. The substance is a colourless viscid liquid, b. p. 135°/20 mm. (Found: C, 45·2; H, 9·2. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%). Heated under atmospheric pressure, it decomposed before boiling and a mixture of products was left from which on distillation (314—320°) a fraction was obtained having the m. p. and solubilities of ethylenecarbamide (E. Fischer and Koch, *Annalen*, 1886, **232**, 227); the same substance is formed when a solution of carbethoxyethylenediamine in dilute aqueous soda is kept for a few days. But the pure compound may be kept for weeks, or repeatedly distilled under a low pressure, without ring closure occurring. On exposure to air the substance absorbs carbon dioxide and water and ultimately gives crystals of an addition compound, $2C_5H_{12}O_2N_2,CO_2$, which is best prepared by passing carbon dioxide into an ethereal solution. The addition compound is soluble in water and alcohol, melts, when heated rapidly, at 102—103°, but decomposes slowly at lower temperatures (Found: C, 43·0; H, 7·8. $C_{11}H_{24}O_6N_4$ requires C, 42·9; H, 7·8%). With carbon disulphide in ethereal solution the carbethoxy-compound reacts, but without heat evolution, to produce a compound quite unlike that given by carbethoxypiperazine in being very hygroscopic and soluble in alcohol. It has not yet been obtained pure enough for analysis.

N-*Benzoyl*-N′-*carbethoxyethylenediamine*,

$$C_6H_5\cdot CO\cdot NH\cdot C_2H_4\cdot NH\cdot CO_2Et,$$

is sparingly soluble in water and readily soluble in the common solvents and crystallises from dilute alcohol in clusters of small needles, m. p. 130° (Found: C, 60·8; H, 6·8. $C_{12}H_{16}O_3N_2$ requires C, 61·1; H, 6·8%).

N-*Toluenesulphonyl*-N′-*carbethoxyethylenediamine*,

$$C_7H_7\cdot SO_2\cdot NH\cdot C_2H_4\cdot NH\cdot CO_2Et,$$

is almost insoluble in water, soluble in the common solvents, and is best recrystallised from ether; m. p. 66° (Found: C, 50·3; H, 6·3. $C_{12}H_{18}O_4N_2S$ requires C, 50·4; H, 6·3%).

N-*Toluenesulphonylethylenediamine* was prepared by boiling the preceding compound for 2 hours with 10% alcoholic potassium hydroxide. After removal of the alcohol and neutralisation the substance separates slowly in fine needles, or can be extracted by chloroform. It is sparingly soluble in water and ether, and easily soluble in chloroform and benzene. Recrystallised from benzene, it melts at 121° (Found: C, 50·3; H, 6·4. $C_9H_{14}O_2N_2S$ requires C, 50·5; H, 6·6%).

Ethyl N'-*carbethoxyethylenediamino*-N-*acetate*,

$$EtO_2C\cdot NH\cdot C_2H_4\cdot NH\cdot CH_2\cdot CO_2Et,$$

was prepared from carbethoxyethylenediamine under the conditions given (p. 48) for the preparation of the corresponding piperazine derivative. But on attempting to distil the ester, decomposition occurred and distillation did not commence until 217°/21 mm. was reached; the product then obtained had properties different from those of the original ester. This was therefore hydrolysed, without previous distillation, to the *hydrochloride* of β-aminoethylglycine, $H_2N\cdot C_2H_4\cdot NH\cdot CH_2\cdot CO_2H,2HCl,2H_2O$ (Found: Cl, 31·2; loss over P_2O_5, 15·8. $C_4H_{10}O_2N_2,2HCl,2H_2O$ requires Cl, 31·2; H_2O, 15·9%). The salt loses both hydrogen chloride and water at 105° and dehydrates only slowly over sulphuric acid.

β-*Aminoethylglycine* was prepared from the hydrochloride under the conditions described on p. 48, and was obtained by precipitation with alcohol as an excessively hygroscopic substance, m. p. 144°, sparingly soluble in hot alcohol, insoluble in other organic solvents (Found: C, 40·8; H, 8·6. $C_4H_{10}O_2N_2$ requires C, 40·7; H, 8·5%). At the same time an alcohol-soluble substance was produced, of which sufficient for identification has not yet been obtained.

The authors wish to express their gratitude to Professor W. P. Wynne for providing one of them (V. M. T.) with facilities for carrying out part of this work in the Chemical Laboratory of the University of Sheffield, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the cost of the investigation.

Royal Holloway College,
Englefield Green, Surrey. [*Received, November 19th*, 1928.]

IX.—*The Infra-red Emission Spectra of Flames in Nitrous Oxide.*

By Charles Reynolds Bailey and Kun-Hou Lih.

The combustion of certain gases in an atmosphere of nitrous oxide has been described by Barratt (*Proc. Roy. Soc.*, 1920, *A*, **98**, 40), Dixon and Higgins (*Fuel*, 1926, **6**, 232) and others. Reiss (*Z. physikal. Chem.*, 1911, **76**, 560) and Reiss and Waldbauer (*ibid.*, 1913, **85**, 62) have also utilised nitric oxide as the supporting atmosphere. All these authors have been struck by the characteristic appearance of the flames, their enlarged size, the increased

illumination, and the numerous zones. Reiss showed ammonia, hydrogen cyanide, and formaldehyde to be present in the interconal space, and Barratt obtained spectroscopic evidence of the water vapour, ammonia, and cyanogen bands under the appropriate conditions. The ready decomposition of nitrous oxide at temperatures above 700° has justified the assumption that, as far as the end products are concerned, the combustible gas burns in the oxygen furnished by this decomposition. Our examination of such flames by infra-red spectroscopy supports the assumption in general, but we have obtained evidence of a *striking anomaly in the case of the hydrogen flame.*

EXPERIMENTAL.

Apparatus.—A Hilger constant-deviation spectrometer (type D 42), fitted with a rock-salt prism, was used in conjunction witl a thermopile–galvanometer combination. The galvanometer wa of the Downing pattern (*J. Sci. Inst.*, 1926, **3**, 331) and was prc tected from magnetic disturbances by a mu-metal shield (A. V. Hil *ibid.*, p. 335). Mechanical interference was largely eliminate by supporting the instrument on a large wooden block resting on brick pillar let into the ground, and the inertia of the whole wa greatly increased by the use of the soft-iron shields associated wit the Paschen instrument. The sensitivity was of the order ($2{\cdot}5 \times 10^{-10}$ amp. per mm. deflexion at a scale distance of 1 metr The work was carried out in a constant-temperature room wit double walls; the spectrometer was enclosed in a felt-covered bo of which the thermal capacity was increased by means of a larg stoppered bottle full of water: the temperature of the enclosu was checked at intervals and found to be constant at 18°. Tl drum was manipulated from a distance and read by means of telescope. The instability of zero due to the adiabatic compressio and expansion of the atmosphere was reduced to a minimum l coupling a similar thermopile in an opposed sense to the recordi instrument inside the case. The gases were burned in a cupboa and viewed by the spectrometer through parallel slits in two lar pieces of tin plate, local heating in the box thus being prevente The work was carried out between the hours of 11 p.m. and 5 a.

The spectrometer was calibrated in the following manner: T instrument was set on the sodium lines 0·5893 μ, very narrow sl being used; this setting gave concordant results on bench marks the further infra-red with those obtained by using the helium l 0·588 μ. As a check on the drum graduations, additional maxi were determined: these included the helium bands at 1·08 a 2·06 μ from a gaseous discharge lamp fitted with a quartz wind and the water vapour emission bands at 2·81, 5·32, and 6·60 μ fr

a hydrogen flame in air, as determined by Paschen (*Ann. Physik*, 1894, **53**, 334). With these precautions, the carbon dioxide maximum in the Bunsen flame was obtained at 4·46 μ: the generally accepted value of 4·40 μ is probably too low, but inasmuch as the drum, in the type of instrument used, is engraved with reference to values of the refractive index of rock-salt uncorrected for temperature changes, too much stress cannot be placed on this. With a slit width of 0·25 mm. for both collimator and thermopile, the average deflexion for this maximum at 1·5 metres scale distance was 50 cm. The value of the slit width in terms of range of spectrum varies over the region examined and is indicated by hatched lines above the curves; the separate maxima are uncorrected for slit width.

The gases were burned at a 4-mm. silica jet in a vessel of Pyrex glass of the form shown in Fig. 1, the window A being of rock-salt. This shape of tube was chosen in order to avoid emission from the heated walls, and for the same reason the tip of the silica jet was kept below the level of the window.

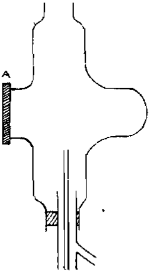


FIG. 1.

Results and Discussion.

The normal spectrum derived from a flame in the infra-red is that of the resultants and not of the reactants. The gases studied in the present research include hydrogen, carbon monoxide, and coal gas; consequently the anticipated spectra are those of water vapour and carbon dioxide. This experimental fact may be due to the condition that generally the supporting atmosphere consists of oxygen or air, both of which are non-polar and without a characteristic infra-red spectrum. If the conditions were reversed and, say, oxygen burnt in an atmosphere of carbon monoxide, it might be possible by thermal stimulation to obtain an emission spectrum from both reactants and resultants. It will be seen that in the case f hydrogen burning in nitrous oxide we have been able to obtain spectrum which will admit of the above suggestion as a partial xplanation.

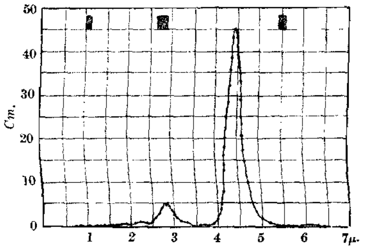
Two methods were adopted for burning the gases: in one the ases were premixed with nitrous oxide in a Y-tube, and in the other he combustible gas was burned in an atmosphere of nitrous oxide. Iydrogen and nitrous oxide were obtained from cylinders, and arbon monoxide was prepared by the action of warm sulphuric cid on formic acid; the gases were roughly dried by passing over a

long column of phosphoric oxide. Observations of the energy curves were made at intervals of 0·1 μ, except in the neighbourhood of each peak maximum, for which the interval was 0·05 μ, or less; the process adopted was to make each reading a difference observation by the use of a shutter.

Carbon monoxide. The same spectrum is obtained whether the gas is premixed with nitrous oxide or burned in the supporting atmosphere, and is the normal carbon dioxide emission spectrum shown in Fig. 2. The higher temperature of the flame produces shifts in the position of the bands and a characteristic decrease in the ratio of their relative intensities (compare Garner and Johnson,

FIG. 2.

Carbon monoxide burning in nitrous oxide.



Phil. Mag., 1927, **3**, 97). The data are summarised in Table I, which includes the corresponding absorption values as determined by Schaefer and Philipps (*Z. Physik*, 1926, **36**, 641). The intensities

TABLE I.

	Wave-length. (1).	(2).	Ratio of intensities (2)/(1).
Emission in air	2·84 μ	4·46 μ	10·1
,, N_2O	2·88	4·50	9·0
Absorption	2·72	4·25	28·5

are assumed to be roughly measured by the galvanometer throw for the peak maximum.

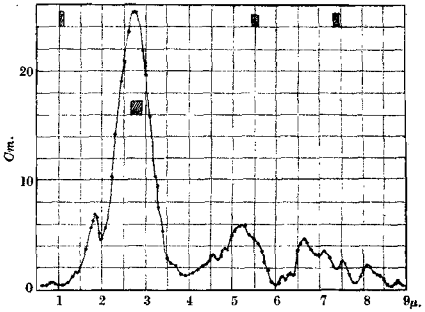
Coal gas. Here again the spectra obtained in both cases are the normal water vapour and carbon dioxide emission curves superimposed, but with slight shifts in the position of the maxima. A detailed consideration of these is therefore omitted.

Hydrogen. When the two gases are premixed, the norms

emission spectrum of water vapour is obtained: the energy curve is given in Fig. 3, and may be compared with that given by Paschen (*loc. cit.*) for the hydrogen flame in air. The flame, however, is complex and possesses at least five zones.

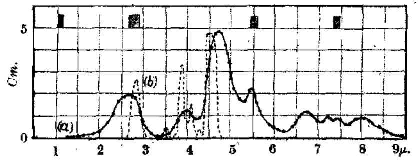
FIG. 3.

Hydrogen premixed with nitrous oxide.



If, now, the hydrogen is burned at the jet (see Fig. 1) in a supporting atmosphere of nitrous oxide, a very different spectrum appears and is shown in Fig. 4, curve (*a*). For the analysis of this, we must refer (i) to the absorption spectrum of nitrous oxide as determined

FIG. 4.



(a) ———— *Hydrogen burning in an atmosphere of nitrous oxide.*
(b) .... *Absorption spectrum of nitrous oxide (Warburg and Leithäuser).*

by Warburg and Leithäuser (*Ann. Physik*, 1909, **28**, 313), whose results are given in Fig. 4, curve (*b*), the chief maximum at 4·47 μ having been afterwards resolved into a Bjerrum doublet by von Bahr (*Verh. deut. physikal. Ges.*, 1913, **15**, 710); and (ii) to the

emission and absorption curves for water vapour as given by Paschen (*loc. cit.*) and Hettner (*Ann. Physik*, 1918, **55**, 476). The data for the outstanding peaks (in μ) of the spectra involved are collected in Table II.

TABLE II.

Emission	Hydrogen in N_2O ...	2·76	4·00	4·75	—	5·49	6·75	7·50	8·00
	Hydrogen in air......	2·75	—	—	5·32	—	6·70	7·50	8·10
Absorption	Water vapour	2·66	—	—	5·95	—	6·51	7·45	8·20
	Nitrous oxide	2·88	3·89, 4·05	4·47	—	—	—	—	—

The following deductions can be made concerning the new spectrum: (1) the broad band at 2·76 μ may be attributed to a combination of the respective water vapour and nitrous oxide bands; (2) the band at 4·00 μ is the emission analogue of the nitrous oxide absorption bands at 3·89 and 4·05 μ, the dispersion of rock-salt in this region being insufficient to separate these; (3) nitrous oxide has a powerful absorption band at 4·47 μ; it seems reasonable tc ascribe the emission band at 4·75 μ to this substance, the shift ir position with increase in temperature being of the order obtainec with carbon dioxide; (4) the appearance of a maximum at 5·49 μ may be due to absorption by hot water vapour at 5·32 μ; and finall (5) the peaks from 6·5 to 9·0 μ present most of the characteristic of the water-vapour spectrum, but upon this another spectrum i imposed which, with the resolution available, is indistinguishable.

The new spectrum does not occur with carbon monoxide, or wit coal gas in either mode of burning, and it is absent in the case c hydrogen premixed with nitrous oxide. Its production may ther fore be attributed to some form of stimulation by the burnir hydrogen molecules, and, since it does not appear in the coal-ga flame, it is probably inhibited by carbon monoxide and hence tl excitement is not merely thermal.

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, October 10th*, 1928.]

X.—*Carbon Sulphidoselenide.*

By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, a PERCY LUCOCK ROBINSON.

IN the course of attempts to prepare carbon diselenide, carb disulphide was passed over heated ferrous selenide, in the hope tl a complete replacement of sulphur by selenium would occ Although this has not been realised, a partial replacement occ

whereby some of the carbon disulphide is converted into carbon sulphidoselenide, CSSe.

Our knowledge of this interesting compound has rested hitherto entirely on the work of Stock and Willfroth (*Ber.*, 1914, **47**, 144), who prepared it by striking an arc under liquid carbon disulphide between poles of carbon containing selenium. We have, therefore, prepared a quantity of this substance by the new method here described, purified it carefully, and investigated further both its physical properties and some of its chemical reactions. Besides redetermining some of the physical constants given by Stock and Willfroth, whose data we are able generally to confirm, we have determined for the first time the coefficient of expansion, the vapour density, and the surface tension.

Little was known of the chemical properties of carbon sulphidoselenide. The data here recorded afford evidence that, though it is markedly less stable than carbon disulphide, it is similarly constituted. Attempts to prepare analogues of the thiocarbonates have failed, but *compounds* of carbon sulphidoselenide with phenylhydrazine and with aniline have been obtained. Under certain conditions the reaction of the sulphidoselenide with ammonia yields compounds which appear to be highly polymerised and are difficult to characterise.

Other attempts to prepare carbon diselenide by striking arcs between carbon rods both in hydrogen selenide and in selenium vapour or between a compressed mixture of carbon and selenium were unsuccessful.

EXPERIMENTAL.

Preparation.—Ferrous selenide, prepared by heating the elements together, was packed into an inclined silica tube 22″ long and 2″ in diameter, electrically heated to 650°. The upper end of the tube carried a tap funnel with drop indicator, from which carbon disulphide was delivered at the rate of about 1 litre in 12 hours; the lower end of the tube was connected to a condenser. The condensate, on fractionation through a 60-inch, bead-filled, glass column, left about 0·5% of a deep yellow liquid as residue. This, when sufficient had been collected, was again repeatedly fractionated through the same column and thus yielded a middle fraction of pure carbon sulphidoselenide (Found: C, 9·7; S, 26·8; Se, 63·4. Calc.: C, 9·8; S, 26·0; Se, 64·2%).

Physical Properties.—Carbon sulphidoselenide is a deep yellow liquid, b. p. 83·90—83·95°/749·2 mm.; it is oily and moderately viscous and only partly wets glass. By the use of glass Ostwald–Sprengel pyknometers of about 10 c.c. capacity, the following values of the density at various temperatures were obtained: $d_{4^\circ}^{t^\circ}$ =

1·9874; $d_{4°}^{20°} = 1·9777$; $d_{4°}^{30°} = 1·9678$; $d_{4°}^{40°} = 1·9484$ (compare $d_{4°}^{20°} = 1·979$, recorded by Stock and Willfroth, *loc. cit.*); hence the mean coefficient of cubical expansion over the range 20—40° is $3\alpha = 0·000996$.

The vapour density, determined by Dumas's method in glass bulbs of about 150 c.c. capacity, was 129·2, 129·3, and 126·1, at 100°, 150°, and 200°, respectively (Calc.: 123·2).

These results were confirmed by cryoscopic determinations of the molecular weight, which gave 128·7 in benzene and 135·7 in bromoform solutions.

Owing to the reluctance of carbon sulphidoselenide to wet glass, attempts to determine its surface tension by the method of capillary rise were quite inconclusive. With the same sample at the same temperature (20°), the difference in height of the liquid in the same two capillary tubes at different settings varied between 5·84 mm. and 8·02 mm., and the maximum value given by this method was $\gamma = 39·70$ dynes per cm., which must be regarded as low. On the other hand, the method of maximum bubble pressure gave constant and reproducible results: $\gamma = 40·44$ dynes per cm. at 20°, whence the molecular parachor $M\gamma^{\frac{1}{4}}/D = 156·4$. Deducting from this value the parachors of carbon (4·8), sulphur (46·5), and of two double bonds (2 × 23·2), we obtain 58·7 as the parachor of selenium. This value is rather lower than that found for the element in selenophen (Briscoe and Peel, J., 1928, 1741) but clearly indicates that carbon sulphidoselenide has the constitution Se=C=S.

Chemical Properties.—The vapour of carbon sulphidoselenide is lachrymatory and causes violent irritation of the nasal mucous membrane; when largely diluted with air it has a disgusting odour. Stock and Willfroth reported that the liquid decomposed on exposure to sunlight and on keeping, but we have found that, although it appears to be slightly affected by sunlight, it remains entirely unchanged on being kept in the dark. This difference in stability suggests that our product may be rather purer than that obtained by Stock and Willfroth, and this may explain the slight difference in density (*vide supra*).

Carbon sulphidoselenide is immiscible with water, but freely soluble without decomposition in ethyl alcohol, benzene, bromoform, acetone, and other organic solvents. Sulphur is very sparingly soluble and selenium is insoluble in the liquid. In marked contrast with carbon disulphide, the liquid sulphidoselenide is non-inflammable, but when warmed its vapour burns with the intense blue flame typical of selenium compounds. At the ordinary temperature it does not react with hydrogen sulphide or hydrogen selenide, but it is readily reduced by zinc and hydrochloric acid to yield these gases.

In contact with saturated aqueous ammonia, after several hours at 15° or in a few minutes at 80°, carbon sulphidoselenide yields a yellow solid which, being insoluble in all solvents and decomposing on heating, could not be purified. Various preparations, washed with water, alcohol, and ether, and dried on a porous plate, gave S from 5·5—10·7% and Se from 52—70%, and on boiling with caustic soda, dissolved completely with evolution of ammonia. The material was slowly but wholly soluble in boiling aqueous ammonia, yielding a blood-red solution, which, when poured into hydrochloric acid, evolved hydrogen sulphide and deposited an orange-red gelatinous precipitate. This precipitate, after being washed with water, alcohol, and ether, and dried, gave Se from 61·4—91·1%, contained no sulphur, easily decomposed on heating, and was insoluble. Attempts to prepare compounds analogous to the thiocarbonates by interaction of the sulphidoselenide with aqueous sodium sulphide, ammonium polysulphides, or caustic soda gave only blood-red solutions from which no crystalline product could be obtained; these solutions when acidified gave similar gelatinous precipitates.

The action of gaseous ammonia on a solution of carbon sulphidoselenide in absolute alcohol produced a considerable rise of temperature and yielded a blood-red solution from which a red amorphous solid was later suddenly precipitated. After being washed with alcohol and ether and dried on porous tile, this product was obtained as a fine brick-red powder containing neither sulphur nor nitrogen; it decomposed on heating, was insoluble in all solvents, and was not attacked by caustic soda solution (Found : Se, 86·9, 88·9, 88·0, 90·0 in various samples; C, 5·6; H, 1·9% in one sample).

In absolute alcohol carbon sulphidoselenide and phenylhydrazine react with evolution of heat, and after about an hour light greenish-yellow, tabular crystals separate. After being washed with alcohol and ether and dried on porous tile, these melt at 98° on rapid heating, but are unstable and on keeping become first brown and later black, with separation of selenium [Found : S, 8·8; C, 41·4; H, 4·25; N, 15·1; Se, 23·7. $(C_6H_5{\cdot}NH{\cdot}NH_2)_2,CSSe$ requires S, 9·4; C, 46·0; H, 4·7; N, 16·5; Se, 23·3%]. This *compound*, therefore, appears to be analogous to that formed by phenylhydrazine and carbon disulphide (Fischer, *Annalen*, 1877, **190**, 114).

Carbon sulphidoselenide, dissolved in alcohol, was treated with aniline in the same solvent and kept for 2 days, during which period there was a continuous evolution of the hydrides of sulphur and selenium. The precipitate of fine, white, crystalline plates, mixed with a little grey selenium, was filtered off, washed with alcohol and ether, and extracted with cold acetone. The extract on

evaporation under reduced pressure yielded fine white plates, m. p. 164° [Found : C, 61·1; H, 4·8; N, 11·2; S, 6·75. $(C_6H_5{\cdot}NH)_4CSSe$ requires C, 61·1; H, 4·9; N, 11·4; S, 6·5%]. The *compound*, which is more stable in air than the phenylhydrazine derivative, is not analogous to the product formed by aniline and carbon disulphide, *viz.*, $(NHPh)_2CS$ (Losanitsch, *Ber.*, 1891, **24**, 3021).

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research which has enabled one of us (*J. B. P.*) to take part in this work.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, October 10th*, 1923.]

XI.—*The Reaction between Ferric Sulphate Solution and Cuprous Sulphide.*

By LAWRENCE WHITBY.

THE reaction between ferric sulphate solution and cuprous sulphide has been investigated by Thomas (*Metallurgie*, 1904, **1**, 8) and Thompson (*Electrochem. Ind.*, 1904, **2**, 228). Using excess of acid ferric sulphate solution, at 60—65° and 80°, respectively, each arrived at the following equation :

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S \quad . \quad . \quad (1)$$

In order to obtain data as to the reaction (if any) that occurs at the ordinary temperature, the action of hydrogen sulphide (obtained from aluminium sulphide and water) upon electrolytic copper foil was used to prepare cuprous sulphide (Found : Cu, 80·26; S, 21·1. Calc. : Cu, 79·86; S, 20·1%), small quantities of which were immersed for 15 minutes in 10 c.c. of ferric sulphate solution (containing 40 g. of anhydrous ferric sulphate and 100 g. of sulphuric acid per litre). The black residue was collected on a Gooch filter, washed rapidly with cold water, dried at 110°, and weighed (Found : Cu, 67·8; S, 34·2. Calc. for CuS : Cu, 66·5; S, 33·5%). Carbon disulphide extraction showed the absence of free sulphur. Hence the reaction at the ordinary temperature may be expressed thus :

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4 \quad . \quad . \quad (2)$$

This equation requires that the residue of cupric sulphide should be 60·0% of the original cuprous sulphide. Actual experiments, in which 0·0264 g. and 0·1968 g. of cuprous sulphide were employed, yielded, respectively, 56·4 and 52·7% of cupric sulphide; these low values may be explained, however, by the great ease of oxidation of

cupric sulphide. Equation (2) was further confirmed by determining the amounts of ferric sulphate solution reduced by known weights of cuprous sulphide, the results obtained agreeing exactly with those calculated from this equation.

It was found, however, that prolonged exposure of the cupric sulphide to ferric sulphate solution caused a further oxidation, with dissolution of copper and production of free sulphur. It is highly probable that this reaction is

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S \quad . \quad . \quad . \quad (3)$$

as actually found by Thompson (*loc. cit.*) to take place at 80°. Hence, although the earlier workers were unable to detect reaction (2), presumably by reason of its increased velocity at the higher temperatures, there is little doubt that the total reaction (1) really consists of stages (2) and (3) under their conditions also.

For permission to publish these results, the author is indebted to Professor G. T. Morgan, F.R.S.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX. [*Received, November 22nd, 1928.*]

XII.—*Anthoxanthins. Part VIII. A Synthesis of Morin and of 5 : 7 : 2′ : 4′-Tetrahydroxyflavone.*

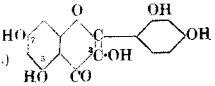
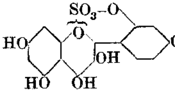
By ROBERT ROBINSON and KRISHNASAMI VENKATARAMAN.

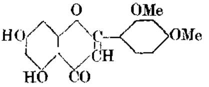
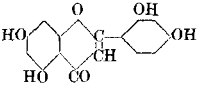
THE formula $C_{15}H_{10}O_7$ was first assigned to morin, one of the colouring matters of old fustic (the wood of *Chlorophora tinctoria*, Gaudich), by Loewe (*Z. anal. Chem.*, 1875, **14**, 112), and the accepted constitution (I) of the flavonol rests on the researches of Bablich and Perkin (J., 1896, **69**, 792) and on the synthesis by Kostanecki, Lampe, and Tambor (*Ber.*, 1906, **39**, 625). That synthesis did not proceed at all smoothly and therefore it seemed well to include morin in the scope of the application of the more convenient methods of synthesising flavones that have been developed in this series of papers.*

ω-Methoxyphloracetophenone (Slater and Stephen, J., 1920, **117**, 309) was heated with 2 : 4-dimethoxybenzoic anhydride and sodium 2 : 4-dimethoxybenzoate at 180—185°, and the product hydrolysed;

* The earlier parts (J., 1924, **125**, 2192; 1925, **127**, 181, 1969, 1974; 1926, 2334, 2336, 2344) of the investigation were not numbered as such and have dealt *inter alia* with the syntheses of galangin, galangin methyl ether, myricetin, datiscetin, kaempferol, fisetin, quercetin, kæmpferide, *iso*rhamnetin, pratol, chrysin, and acacetin. In view of the considerable extension of the work which is contemplated, it appears desirable to indicate the connexion between these otherwise isolated papers.

the *morin* 3 : 2′ : 4′-*trimethyl ether* obtained, on demethylation in the usual manner, yielded morin.

(I.)   (II.)

(III.)   (IV.)

Perkin and Pate (J., 1895, **67**, 649) showed that morin forms an abnormal sulphuric acid compound, $C_{15}H_{10}O_7,SO_3$, and in view of the fact that other flavonols, *e.g.*, fisetin, quercetin, rhamnetin, and myricetin, give normal sulphates, it is apparent that the hydroxyl group in position 2′ is concerned. Hence the formula (II) probably correctly represents anhydromorin sulphate. The recovery of morin from the derivative shows that no closure of a coumaran ring occurs.

Dunstan and Henry (*Phil. Trans.*, 1901, **194**, 515) suggested that lotoflavin, obtained by the hydrolysis of the cyanogenetic glucoside lotusin, might be 5 : 7 : 2′ : 4′-tetrahydroxyflavone (IV). This flavone has been synthesised by demethylation of its dimethyl ether (III), derived from phloracetophenone by 2 : 4-dimethoxybenzoylation, but it does not appear to be identical with lotoflavin.

EXPERIMENTAL.

2 : 4-*Dimethoxybenzoic Anhydride.*—In the preparation of β-resorcylic acid (Kostanecki, *Ber.*, 1885, **18**, 1985) the isolation by ether extraction can be conveniently replaced by separation of the crystals obtained on acidification of the reaction mixture.

A greatly improved yield of 2 : 4-dimethoxybenzoic acid results when the method of Perkin and Schiess (J., 1904, **85**, 189) for the methylation of β-resorcylic acid is modified as follows. Methyl sulphate and concentrated aqueous sodium hydroxide are added alternately to a well-stirred solution of β-resorcylic acid (75 g.) in 10% aqueous sodium hydroxide (700 c.c.) so that a considerable rise of temperature ensues; the addition is stopped when a neutralised test portion gives no violet coloration on the addition of ferric chloride. The mixture is then boiled for an hour, alcohol (200 c.c.) and sufficient sodium hydroxide to maintain a strongly alkaline reaction being added. The acid obtained on acidification of the

cooled liquid is isolated and crystallised from aqueous acetic acid (yield, 82 g. or 92%; m. p. 108°).

The anhydride was not produced when 2 : 4-dimethoxybenzoic acid was boiled for 24 hours with acetic anhydride. It was at first obtained by the action of 2 : 4-dimethoxybenzoyl chloride (best prepared from the acid by means of thionyl chloride) on 2 : 4-dimethoxybenzoic acid in the presence of ether and pyridine, but the method of D.R.-P. 201325 was found to give much better results. It was advantageous to replace the benzene, prescribed as solvent in the patent, by ether. A solution of thionyl chloride (11·9 g.) in ether (50 c.c.) was gradually added with shaking to a suspension of 2 : 4-dimethoxybenzoic acid (36·4 g.) in ether (50 c.c.) and pyridine (15·8 g.), the whole being cooled in melting ice. After 12 hours, crushed ice and dilute hydrochloric acid were added. The anhydride, which separated, was collected, triturated with much very dilute sodium carbonate solution, washed, and dried (yield, 29 g. or 84%; m. p. 76—79°). It crystallised from benzene–ether, ethyl acetate–ether, or light petroleum in large, colourless, rhombic prisms, m. p. 82° (Found: C, 62·3; H, 5·4. Calc. for $C_{18}H_{18}O_7$: C, 62·4; H, 5·2%).

Morin 3 : 2′ : 4′-*Trimethyl Ether*.—As in the preparation of phloracetophenone (compare J., 1926, 2347), so in the analogous preparation of ω-methoxyphloracetophenone (Slater and Stephen, *loc. cit.*) it is desirable to add zinc chloride and to keep the reaction mixture for a few days in the ice-chest before separating the ketimine hydrochloride. The ketone is best crystallised from aqueous alcohol and the yield is 75—80%.

A mixture of ω-methoxyphloracetophenone (6 g.), 2 : 4-dimethoxybenzoic anhydride (50 g.), and sodium 2 : 4-dimethoxybenzoate (12 g.) was heated at 180—185° for 4 hours. The product was dissolved in boiling alcohol (250 c.c.), a solution of potassium hydroxide (30 g.) in water (50 c.c.) added, and the liquid refluxed for 30 minutes and then diluted with water (1000 c.c.). The passage of carbon dioxide caused the slow precipitation of an amorphous brown powder, which was collected and reprecipitated by carbon dioxide from its solution in 2% aqueous potassium hydroxide (yield, 7·3 g.). The *trimethyl ether* was crystallised from 95% alcohol, containing a little acetic acid (charcoal), and then from aqueous alcohol (charcoal) and was obtained in glistening, pale straw-coloured, stout, long, prismatic needles, m. p. 132° (Found: C, 62·4; H, 4·6. $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). It is moderately readily soluble in most organic solvents on heating, but it is very sparingly soluble in ether and light petroleum. It dissolves in aqueous alkali to yellow solutions and its yellow solution

in concentrated sulphuric acid exhibits a bluish-green fluorescence. The ferric chloride reaction in alcoholic solution is olive-green and addition of lead acetate to an alcoholic solution gives a yellow precipitate.

The pentamethyl ether was obtained by the action of methyl sulphate (4 mols.) and aqueous potassium hydroxide on morin trimethyl ether; the product, twice crystallised from 50% aqueous alcohol, formed colourless feathery needles, m. p. 155—157° (Found: C, 64·3; H, 5·5. Calc. for $C_{20}H_{20}O_7$: C, 64·5; H, 5·4%). The melting point was not depressed on admixture with a specimen of morin pentamethyl ether prepared from morin (Herzig and Hofmann, *Ber.*, 1909, **42**, 155; Perkin and Watson, J., 1915, **107**, 207) and the properties of the two specimens were identical in all respects.

We are greatly indebted to Professor A. G. Perkin, F.R.S., for a specimen of morin from old fustic which has enabled us to make this and other comparisons.

O-2 : 4-*Dimethoxybenzoyl*-O-*acetylmorin* 3 : 2′ : 4′-*Trimethyl Ether*.—This substance was produced in an attempt to prepare *O*-diacetyl-*O*-trimethylmorin. The crude product, from which *O*-trimethylmorin can be obtained as described above, was boiled with an excess of acetic anhydride and a drop of pyridine for 2 hours. The derivative was isolated in the usual manner and crystallised from aqueous alcohol in shining colourless needles, m. p. 170° after shrinking at 167° (*Found*: C, 63·3, 63·1, 63·1; H, 5·0, 5·1, 5·2; MeO, 28·0; $CH_3 \cdot CO$, by the Freudenberg–Weber method, 8·1. $C_{29}H_{26}O_{11}$ requires C, 63·3; H, 4·7; 5MeO, 28·2; $CH_3 \cdot CO$, 7·8%). At the time these micro-analyses were conducted, the values for hydrogen found in many other cases with the same apparatus were about 0·4 unit too high.

It is evident that one of the 2 : 4-dimethoxybenzoyloxy-groups in the original reaction product resists hydrolysis to some extent under the prescribed conditions and that the crude product is a mixture of trimethylmorin and its dimethoxybenzoate.

Morin (I).—A mixture of *O*-trimethylmorin (2·0 g.), hydriodic acid (30 c.c.; *d* 1·7), and acetic anhydride (15 c.c.) was refluxed for 2 hours. The flavonol hydriodide, which separated in minute needles on cooling, was collected, washed with acetic acid, and added to boiling acetic acid (50 c.c.) and after the addition of boiling water (50 c.c.) the whole was quickly filtered; long, pale yellow needles (1·2 g.) separated, m. p. 286—288° after sintering at 281°. The substance was recrystallised from dilute acid without alteration in its properties (Found in material dried at 130° for 6 hours: C, 55·8; H, 3·6. Found after further heating without loss in a high vacuum for 6 hours at 130°: C, 56·0; H, 3·7. $C_{15}H_{10}O_7,H_2O$ requires C,

56·2; H, 3·8%). It thus appears that the substance retains a molecule of water at 130° even in a high vacuum. This behaviour has not been recorded in the case of morin of natural origin. Loewe (*loc. cit.*) states that morin crystallises with $2H_2O$ and loses both molecules of water at 100°.

Our synthetic morin is evidently identical with that of Kostanecki, Lampe, and Tambor (*loc. cit.*), for the latter had a pale yellow colour and m. p. 290° with decomposition. On the other hand, natural morin is nearly colourless and, according to Bablich and Perkin (*loc. cit.*), melts and decomposes at about 300°. These authors recorded new analyses of morin derivatives but not of morin itself.

A very careful comparison of the solubility relations and of the characteristic reactions of morin disclosed no divergences between the natural and the synthetic specimen. We observed in both cases the qualitative solubilities in organic solvents, the yellow colour and bright bluish-green fluorescence of the solutions in sulphuric acid, the dark olive-green ferric chloride reactions in alcoholic solution, and the change to brown on the addition of water, the formation of lead and barium salts and of salts with mineral acids, the behaviour with magnesium and methyl-alcoholic hydrochloric acid, and the colorations obtained on the addition of sodium amalgam to alcoholic solutions. In this case the solutions are at first yellow and exhibit a yellow fluorescence; the colour slowly changes to bright emerald-green and on dilution the solution exhibits a greenish-yellow fluorescence.

A dye-trial comparison showed that the natural and the synthetic specimen gave identical results on cotton printed with aluminium and iron mordants.

We draw the conclusion from our experiments that the substance synthesised is substantially morin, the properties of which are to some extent modified by the presence of small traces of impurities. This difficulty, which has not been encountered previously in the case of a flavonol synthesis, is probably inherent in the demethylation process. A synthesis of morin not involving demethylation as the final stage is projected.

5 : 7-*Dihydroxy*-2′ : 4′-*dimethoxyflavone* (III).—A mixture of phloracetophenone (6 g.), 2 : 4-dimethoxybenzoic anhydride (100 g.), and sodium 2 : 4-dimethoxybenzoate (6 g.) was mechanically stirred at 180—185°, and a further quantity of sodium 2 : 4-dimethoxybenzoate (6 g.) introduced during an hour. The heating was continued for 8 hours, alcohol (350 c.c.) added, and the whole boiled under reflux; a solution of potassium hydroxide (40 g.) in water (50 c.c.) was then introduced and the refluxing continued for

30 minutes. Alcohol was removed by distillation under diminished pressure and the residue was dissolved in water and saturated for several hours with carbon dioxide. The crude flavone, a light brown powder (11·8 g.), was redissolved and reprecipitated (10·9 g.) and then dissolved in boiling acetic acid (200 c.c.) and treated with concentrated sulphuric acid (2 c.c.) and boiling water (100 c.c.). After boiling for a few minutes the liquid was filtered, leaving a residue (A). The filtrate was treated with charcoal and again filtered; on cooling, it slowly deposited pale brown, hexagonal plates and rectangular prisms (2·4 g.) that sintered at about 200° and melted at 245—248°. The *flavone* (III) was best recrystallised from aqueous acetic acid containing a little concentrated hydrochloric acid (charcoal) and was ultimately obtained in pale yellow, woolly needles, m. p. 258—259°. The residue (A) crystallised readily from acetic acid (charcoal), in which it was moderately readily soluble at the boiling point and very sparingly soluble in the cold, in pale yellow, woolly needles, m. p. 258—259° (0·8 g.), identical with the specimen previously obtained (Found: C, 63·5; H, 4·6; MeO, 19·3. Found in a recrystallised specimen dried at 140°: C, 63·4; H, 4·6. $C_{17}H_{14}O_6,0{\cdot}5H_2O$ requires C, 63·2; H, 4·6; MeO, 19·2%). The direct estimation of combined water, the presence of which was proved qualitatively, was vitiated by the sublimation that occurred in a high vacuum at the requisite temperature.

The substance is practically insoluble in boiling water, sparingly soluble in ether, and is moderately readily soluble in boiling alcohol. Alcoholic ferric chloride develops a weak greenish-brown coloration and the solutions in aqueous alkalis are bright yellow. Especially striking is the pure blue fluorescence exhibited by the pale yellow solution in concentrated sulphuric acid.

5 : 7 : 2′ : 4′-*Tetrahydroxyflavone* (IV).—A mixture of 5 : 7 dihydroxy-2′ : 4′-dimethoxyflavone (3·1 g.), acetic anhydride (10 c.c.), and hydriodic acid (20 c.c.; *d* 1·7) was boiled for 3 hours and the deep scarlet hydriodide that crystallised was collected, after cooling, on a sintered glass filter and washed with acetic acid. The residue was dissolved in boiling acetic acid, an equal volume of water added, and the crystalline material thus obtained was acetylated by boiling with an excess of acetic anhydride for 4 hours. The derivative crystallised from alcohol in colourless prisms, m. p. 153—156°; after recrystallisation from ethyl acetate it melted at 159°, but some crystals remained unmelted and complete clearing only occurred at 170°. Evidently this apparently homogeneous substance was a mixture, probably containing some triacetate; the ferric chloride reaction was almost negligible. Tests in the Pregl-Zeisel and the Pregl-Herzig-Meyer apparatus proved the

complete absence of methoxyl. The acetate was hydrolysed by means of boiling dilute aqueous-alcoholic sodium hydroxide. The almost colourless *flavone* produced crystallised from glacial acetic acid or from alcohol in slender fibrous needles which darkened progressively from 300° and melted at 332—335° with further decomposition (Found in material dried at 160°: C, 62·7; H, 3·6. $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%). This isomeride of luteolin differs from it in possessing a much paler yellow colour, just as morin is much more feebly coloured than quercetin; its dyeing properties are similar to those of apigenin. The pale yellow solution in sulphuric acid exhibits a violet-blue fluorescence.

In these and other properties the substance showed little resemblance to lotoflavin, for a specimen of which we are greatly indebted to Dr. T. A. Henry.

Dye trials on aluminium and iron mordants disclosed great divergences, since lotoflavin proved to be a good dyestuff giving shades generally similar to those from flavonols—it was closest to quercetin—whereas the tetrahydroxyflavone had feeble tinctorial properties.

A solution of lotoflavin in sulphuric acid had a vivid bluish-green fluorescence similar to that produced by morin and it may be that this particular specimen was contaminated by morin, the presence of which masked the exhibition of the properties of 5 : 7 : 2′ : 4′-tetrahydroxyflavone.

Quite recently Cullinane, Algar, and Ryan (*Proc. Roy. Dublin Soc.*, separate issue, Nov., 1928) have described a different synthesis of 5 : 7 : 2′ : 4′-tetrahydroxyflavone (bright yellow plates, decomposing above 270° and giving a greenish-blue fluorescence in sulphuric acid), which, they consider, closely resembles lotoflavin. Definite evidence of identity was not obtained.

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XIII.—*Anthoxanthins. Part IX. Syringetin.*

By TOM HEAP and ROBERT ROBINSON.

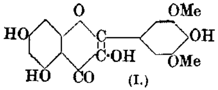
THE synthesis of myricetin 3′ : 5′-dimethyl ether (I) was originally undertaken in order to attempt its reduction to the anthocyanidin malvidin (Willstätter and Mieg, *Annalen*, 1915, **408**, 122), but this has not been carried out because the preparation of the flavonol was found to be difficult and the substance was not accessible in adequate amount. Moreover, we have been unable to reduce kaempferol, synthesised by the method of Robinson and Shinoda (*J.*, 1925, **127**,

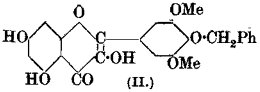
1980), to pelargonidin salts either directly, following the method of *Willstätter and Mallison* (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769) for the reduction of quercetin, or indirectly by the acetylating reduction process which succeeded with rhamnetin (Robertson and Robinson, J., 1927, 2196). The products doubtless contained a small proportion of pelargonidin, but it was mixed with so much impurity that we were unable to isolate the pure anthocyanidin.

There was no reason to suppose that the myricetin dimethyl ether (dimethoxykaempferol) would behave differently from kaempferol and meanwhile the synthesis of malvidin was effected in another way (Bradley and Robinson, J., 1928, 1541).

In view, however, of the wide distribution of syringidin (malvidin) in nature (Karrer and Widmer, *Helv. Chim. Acta*, 1927, **10**, 5) and of the occurrence of other natural products, such as sinapin, containing the syringic grouping, $C{\cdot}C_6H_2(OH)(OMe)_2$ (4 : 3 : 5), and also in view of the fact that kaempferol, quercetin, *iso*rhamnetin, and myricetin correspond to pelargonidin, cyanidin, peonidin, and delphinidin, respectively, it seemed of interest to place on record the properties of myricetin 3′ : 5′-dimethyl ether, the flavonol corresponding to syringidin.

It seems probable that this substance will ultimately be isolated from natural sources and we propose to term it *syringetin* (I).


(I.)


(II.)

The method which has been developed for the preparation of this flavonol is based on that which we have already used for the synthesis of *iso*rhamnetin (J., 1926, 2336) and consists essentially in the syringoylation of ω-benzoyloxyphloracetophenone,

$$C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2{\cdot}OBz,$$

and hydrolysis of the product.

It was necessary to protect the phenolic hydroxyl group of syringic acid before an anhydride could be formed, and since the use of *O*-benzoylsyringic anhydride did not give satisfactory results we employed *O*-benzylsyringic anhydride in its stead.

When ω-benzoyloxyphloracetophenone was heated with sodium *O*-benzylsyringate and *O*-benzylsyringic anhydride and the product hydrolysed by alkali, *syringetin 4′-benzyl ether* (II) was obtained. Further hydrolysis by means of alcoholic hydrochloric acid yielded syringetin. This was characterised by conversion into a *tetra-acetyl* derivative and on methylation it furnished myricetin hexamethyl ether. At an earlier stage of the work myricetin

3′ : 4′ : 5′-trimethyl ether was prepared, but the requisite conditions for the partial demethylation to syringetin could not be ascertained.

EXPERIMENTAL.

3 : 4 : 5-*Trimethoxybenzoic Anhydride*.—The following method, based on one suggested in D.R.-P. 201325 for the preparation of *o*-acetoxybenzoic anhydride, is more convenient and gives a better yield of a purer product than that described by Kalff and Robinson (J., 1925, **127**, 181). A mixture of finely powdered *O*-trimethylgallic acid (120 g.), dry ether (800 c.c.), and pyridine (75 c.c.) was cooled in melting ice, and thionyl chloride (51 g.; 1·5 mols.) gradually added with shaking. After a few hours (at 0°), crushed ice was added and the mixture was agitated for about 10 minutes and then filtered. The solid was triturated successively with dilute hydrochloric acid, dilute aqueous sodium carbonate, and water, all ice-cold, and then dried in a vacuum (yield, 103 g. or 89·6%; m. p. 159—160°). A similar method applied to anisic acid (100 g.) gave anisic anhydride (92 g.), m. p. 98—99°.

Myricetin 3′ : 4′ : 5′-*Trimethyl Ether*.—An intimate mixture of ω-benzoyloxyphloracetophenone (Heap and Robinson, *loc. cit.*) (9·5 g.; 1 mol.), sodium *O*-trimethylgallate (11·5 g.; 1·5 mols.), and 3 : 4 : 5-trimethoxybenzoic anhydride (94 g.; 7 mols.) was heated (oil-bath at 180—185°) for 9·5 hours and mechanically stirred. The melt, which became deep orange-brown, was dissolved in boiling alcohol (550 c.c.), a solution of potassium hydroxide (33 g.) in water (50 c.c.) was then slowly introduced, and after boiling gently for 30 minutes the alcohol was removed by distillation and the residue dissolved in water. The filtered solution was diluted to 1100 c.c., saturated with carbon dioxide, kept for 12 hours, and again saturated with the gas. The yellow precipitate obtained was dried at 100° (8·8 g.), and 7·9 g. of it, crystallised from acetic acid (charcoal), gave clusters of pale yellow needles (5·7 g.), m. p. 290—293°. The flavonol also crystallised from alcohol in extremely fine, long, pale yellow needles, m. p. 290—293° (Found: C, 59·8; H, 4·7. $C_{18}H_{16}O_8$ requires C, 60·0; H, 4·4%).

Myricetin 3′ : 4′ : 5′-*trimethyl ether* is very sparingly soluble in the simple alcohols, chloroform, acetone, or ethyl acetate and is almost insoluble in benzene, ether, light petroleum, and water; it is not very readily soluble in boiling acetic acid. Addition of mineral acids to a suspension in acetic acid gives deep yellow solutions; in the case of hydrobromic and sulphuric acids the solutions exhibit a green fluorescence, but the deep yellow solution obtained with hydrogen chloride is non-fluorescent. The yellow solution in concentrated sulphuric acid exhibits a weak green fluorescence.

The flavonol gives an intensely yellow solution in aqueous alkali and the addition of ferric chloride to an alcoholic suspension produces a deep brownish-olive-green coloration. The lead salt is a deep yellow precipitate.

The O-*triacetyl* derivative was obtained by the action of boiling acetic anhydride (20 c.c.) and a drop of pyridine on the flavonol (0·5 g.) during 1 hour. It crystallised from alcohol in very fine, nearly white needles, m. p. 195—195·5° (Found : C, 59·0; H, 4·8. $C_{24}H_{22}O_{11}$ requires C, 59·3; H, 4·5%). The substance is sparingly soluble in alcohol, moderately readily soluble in acetic acid and benzene, and very sparingly soluble in ether. The ferric chloride reaction in alcoholic solution was negative.

Action of Fuming Sulphuric Acid on Myricetin Trimethyl Ether.—Syringic acid can be conveniently obtained by the partial demethylation of O-trimethylgallic acid by means of 20% fuming sulphuric acid at 40° (Bogert and Isham, *J. Amer. Chem. Soc.*, 1914, **36**, 517; Bogert and Ehrlich, *ibid.*, 1919, **41**, 799) and we therefore attempted the preparation of syringetin analogously.

Finely powdered myricetin trimethyl ether (4·5 g.) was added during 1·5 hours to fuming sulphuric acid (30 c.c. of 20%), mechanically stirred and kept below 40°; the mixture was then maintained at 40—44° for 30 minutes. Next day the deep red liquid was added to water (150 c.c.), but nothing separated. Sulphuric acid (115 c.c.) was then added and a bright yellow solid was precipitated. This was soluble in aqueous sodium bicarbonate and contained sulphur, so that it was clearly a sulphonic acid, and in an attempt to hydrolyse it the mixture was heated in an oil-bath at 150° and a stream of super-heated steam passed for 7 hours. After cooling, the product was added to water and the solid isolated (4·7 g.). The substance crystallised from methyl alcohol in fine yellow needles which darkened at 310° but did not melt at 330° (Found : C, 46·5; H, 3·4; S, 7·8. $C_{16}H_{12}O_{11}S$ requires C, 46·6; H, 2·9; S, 7·8%). It is evidently a *monomethylmyricetinsulphonic acid* and the presence of an *o*-dihydroxybenzene group is suggested by the intense dark olive-green coloration developed in alcoholic solution on the addition of ferric chloride.

The substance is moderately readily soluble to yellow solutions in methyl and ethyl alcohols, ethyl acetate, or acetone, very sparingly soluble in hot acetic acid and chloroform, and almost insoluble in water and benzene. The yellow solution in concentrated sulphuric acid exhibits a green fluorescence and the aqueous alkaline solutions are orange.

O-Benzoylsyringic Acid and its Chloride.—Benzoyl chloride (125 g.) was added to a solution of syringic acid (118 g.) in aqueous sodium

hydroxide (95 g. in 1600 c.c.), and the mixture shaken until the smell of the chloride had disappeared. The acids were isolated after acidification and unchanged syringic acid and benzoic acid were removed by extraction of the product with successive volumes of hot water (total, 3200 c.c.). The more sparingly soluble residue, a fine white powder, was dried at 100° (yield, 88 g. or 49%). The *acid* crystallised from acetic acid in almost colourless needles, m. p. 229—232° after softening at 215° (Found: C, 63·3; H, 4·8. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%).

The *chloride*, obtained by the action of phosphorus pentachloride, crystallised from light petroleum in clusters of fine needles (36 g. from 40 g. of the acid), m. p. 116·5—118° (Found: C, 60·1; H, 4·5; Cl, 11·0. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1; Cl, 11·1%). On a large scale the use of thionyl chloride was found to be preferable.

The *anhydride* was obtained by following several of the most satisfactory methods, but the products fused variously at temperatures between 200° and 228° and there is some inexplicable difficulty in preparing the pure substance.

Even the crude substance, however, had so high a melting point that a good fluid melt could not be obtained at the stage of the flavonol synthesis and several attempts in this direction failed for this reason. The preparation of galangin was attempted, the temperature of the melt being raised from 165—170° to 200°, but very little of the colouring matter could be isolated as the result of the augmented decomposition which occurred under such conditions. It may be recalled that benzoylvanillic anhydride, successfully applied in the synthesis of isorhamnetin, had m. p. 179—180°.

O-*Benzylsyringic Anhydride*, $[CH_2Ph\cdot O\cdot C_6H_2(OMe)_2\cdot CO]_2O$.—Finely powdered *O*-benzylsyringic acid (144 g.) (Bradley and Robinson, *loc. cit.*) was suspended in an ice-cold mixture of dry ether (500 c.c.) and pyridine (53 g.) and a solution (74 c.c.) of thionyl chloride (37 g.) in ether was added portionwise with vigorous shaking during 1·5 hours. The product (118 g., m. p. 111—113°) was isolated as was trimethoxybenzoic anhydride (above); it crystallised from benzene-light petroleum in long needles, m. p. 112—113° (Found: C, 68·6; H, 5·7. $C_{32}H_{30}O_9$ requires C, 68·8; H, 5·4%).

O-*Benzylsyringic anhydride* is moderately readily soluble in alcohol, acetone, or ethyl acetate, readily soluble in chloroform and benzene, and sparingly soluble in ether and light petroleum.

Syringetin 4′-Benzyl Ether (II).—Benzylsyringic anhydride (110 g.; 7 mols.), sodium benzylsyringate (13·1 g.; 1·5 mols.), and ω-benzoyloxyphloracetophenone (8·0 g.; 1 mol.) were ground together and heated for 9 hours in an oil-bath at 180—185°. The mobile, liquid, deep reddish-brown melt was poured as completely

as possible into alcohol (200 c.c.) and the residue in the flask was chipped out when cold and washed out with hot alcohol (200 c.c.). The whole was then refluxed for 2 hours, a solution of potassium hydroxide (20 g.) in water (30 c.c.) gradually added, and the mixture boiled gently for 30 minutes. The liquid was concentrated under diminished pressure to about 100 c.c., the residue dissolved in water and saturated with carbon dioxide, and the precipitate isolated (10·5 g.). This product could not be crystallised and it was judged to be contaminated with benzylsyringoyl derivatives; it was accordingly boiled for 20 minutes with a solution of potassium hydroxide (5 g.) in alcohol (100 c.c.), and the phenol isolated as before (8·0 g.). This material (7·5 g.) gradually dissolved in boiling acetic acid (200 c.c.) and when kept in the ice-chest the solution deposited a mass of small brown needles (4·8 g.), m. p. 240—242°. The *flavonol* was recrystallised from acetic acid, giving fine brownish-orange needles which were dried at 130—140° for several hours and then had m. p. 240—241° (Found: C, 65·7; H, 4·9. $C_{24}H_{20}O_8$ requires C, 66·1; H, 4·6%). This substance is sparingly soluble in most organic solvents and dissolves in aqueous alkalis to deep yellow solutions. The yellow solution in concentrated sulphuric acid exhibits a dull green fluorescence more intense than that due to myricetin trimethyl ether and less intense than that due to syringetin under the same conditions. An alcoholic solution of the flavonol develops an olive-green coloration on the addition of ferric chloride and gives a flocculent yellow precipitate with lead acetate.

Triacetyl Derivative.—Syringetin 4′-benzyl ether (0·4 g.) was acetylated by means of boiling acetic anhydride (15 c.c.) and a drop of pyridine during 1 hour. Slow crystallisation from acetic acid gave rhombic plates and more rapid separation from the same solvent or from alcohol gave small needles, m. p. 191—194° (Found: C, 64·0; H, 4·8. $C_{30}H_{26}O_{11}$ requires C, 64·1; H, 4·6%). The substance is moderately readily soluble in alcohol, acetone, or acetic acid, sparingly soluble in ethyl acetate, chloroform, or ether, and very sparingly soluble in benzene or light petroleum.

Syringetin (*5 : 7 : 4′-Trihydroxy-3′ : 5′-dimethoxyflavonol*, I).—Unlike *O*-benzylsyringic acid, *O*-benzylsyringetin was not readil[y] de-benzylated by boiling for a short time with concentrated hydro[-] chloric acid, but on prolonged treatment with a boiling mixture o[f] concentrated hydrochloric acid and alcohol a part of the materia[l] was attacked and the unchanged benzyl ether remained undis[-] solved in the acid liquor.

For example, a mixture of *O*-benzylsyringetin (2·3 g.), alcoho[l] (… c.c.), and concentrated hydrochloric acid (100 c.c.) was boile[d] … hours. The insoluble residue (0·75 g.) had m. p. 242—243

and the filtrate, after being concentrated and cooled, deposited brown material (1·3 g.) which crystallised from acetic acid (charcoal) in short, glistening, pale yellow needles. The crystals lost their lustre after being heated for several hours at 130—140° and had m. p. 288—289° after darkening at about 270° (Found in material dried at 160° in a vacuum: C, 58·7; H, 4·1. $C_{17}H_{14}O_8$ requires C, 59·0; H, 4·0%).

Syringetin is moderately readily soluble in methyl and ethyl alcohols, acetone, or acetic acid; it is sparingly soluble in ethyl acetate and chloroform and is insoluble in benzene or light petroleum. The crystals are coloured orange by sulphuric acid and dissolve to a yellow solution exhibiting a green fluorescence; the alkaline solutions are intensely yellow. In dyeing properties and many other respects the substance very closely resembles *iso*rhamnetin, of which it is a methoxy-derivative.

Tetra-acetyl Derivative.—This preparation was carried out like that of the triacetate of *O*-benzylsyringetin and the crude product was crystallised by solution in boiling acetic anhydride and addition of water; when the anhydride was decomposed, the hot liquid was treated with charcoal and filtered. The *derivative* separated in clusters of very slender, white needles, m. p. 224—226° (Found: C, 58·1; H, 4·2. $C_{25}H_{22}O_{12}$ requires C, 58·3; H, 4·3%). The substance is moderately readily soluble in ethyl acetate, chloroform, acetone, or acetic acid, sparingly soluble in the alcohols or benzene, and almost insoluble in ether or light petroleum.

Myricetin Hexamethyl Ether.—Syringetin (0·15 g.) was methylated by the gradual and alternate addition of concentrated aqueous potassium hydroxide and methyl sulphate (5 g.) with shaking; the mixture was finally heated on the steam-bath for 1 hour. The product crystallised from light petroleum in almost colourless needles, m. p. 159—161° (literature, 154—156°). The substance was also prepared for comparison from *O*-tetramethylmyricetin (Kalff and Robinson, *loc. cit.*) and the specimen obtained had m. p. 159—160°. An analysis by the Pregl method gave a low value for carbon and this was overcome by the use of a longer tube, a higher temperature, and a slower combustion (Found: C, 62·5; H, 5·5. Calc. for $C_{12}H_{22}O_8$: C, 62·7; H, 5·5%) (compare Freudenberg, Fikentscher, and Wenner, *Annalen*, 1925, **442**, 314).

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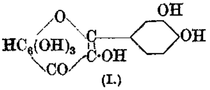
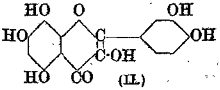
XIV.—*Anthoxanthins. Part X. The Synthesis of Gossypetin and of Quercetagetin.*

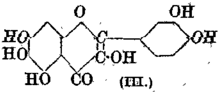
By Wilson Baker, Ryuzaburo Nodzu, and Robert Robinson.

Quercetagetin, a colouring matter of the flowers of the African marigold, *Tagetes patula*, was isolated by Latour and Magnier de la Source (*Bull. Soc. chim.*, 1877, **28**, 337) and closely examined by A. G. Perkin (P., 1902, **18**, 75; J., 1913, **103**, 209); the isomeric gossypetin was isolated by Perkin in 1899 from the flowers of the Indian cotton plant, *Gossypium herbaceum* (J., 75, 826), and a more complete study was published in 1913 (Perkin, J., **103**, 650). Perkin was able to show that the structures of both substances must conform to the formula (I), but it was not possible to determine the situation of the hydroxyl groups in the tetrahydroxybenzene nuclei. The probability that these flavonols are nearly related to quercetin and are indeed hydroxyquercetins (II and III) was commented on, but this attractive view had to be abandoned in the case of one at least of the two colouring matters on account of the synthesis of


(I.)


(II.)

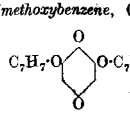
(II) by Nierenstein (J., 1917, **111**, 872), who employed an apparently unambiguous method. The hydroxyquercetin so obtained was stated to be identical with that previously derived from quercetone

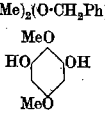

(III.)

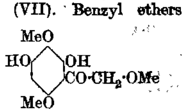
by reduction (Nierenstein and Wheldale, *Ber.*, 1911, **44**, 3487) and comparisons of derivatives confirmed this identity, but it was quite different from gossypetin and from quercetagetin. A remarkable property of this hydroxyquercetin was its ability to yield *iso*quercetone on oxidation by means of *p*-benzoquinone (Nierenstein J., 1915, **107**, 869); thus two isomeric quinones corresponded to a single polyhydric phenol. Our results confirm the work of Perkin in all details, but are irreconcilable with that of Nierenstein (the reference is to the paper of J., 1917, **111**, 872), since we find (*a*) that gossypetin has the formula (*II*); (*b*) that both gossypetin and quercetagetin are derivatives of 1 : 3 : 4 : 5-tetrahydroxybenzene

hydroxyphloroglucinol), and that consequently (c) quercetagetin must be represented by the formula (III).

The synthesis of gossypetin was effected in the following manner. The *tribenzyl* ether of pyrogallol, $C_6H_3(O{\cdot}CH_2Ph)_3$ (IV), was oxidised by means of nitric acid to 2 : 6-*dibenzyloxy*-p-*benzoquinone* (V), this was reduced to the *quinol*, $C_6H_2(OH)_2(O{\cdot}CH_2Ph)_2$ (VI), which was methylated with formation of 2 : 6-*dibenzyloxy*-1 : 4-*dimethoxybenzene*, $C_6H_2(OMe)_2(O{\cdot}CH_2Ph)_2$ (VII). Benzyl ethers


(V.)


(VIII.)


(IX.)

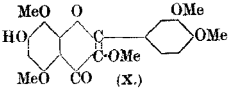
being much more readily hydrolysed than methyl ethers, 2 : 5-*dimethoxyresorcinol* (VIII) was obtained by the action of a mixture of hydrochloric and acetic acids on (VII) at about 65°.

The monomethyl ether of iretol described by de Laire and Tiemann (*Ber.*, 1893, **26**, 2034) should be represented by one of the formulæ (VIII) and (XII). The latter is the 4 : 5-dimethoxyresorcinol of Chapman, Perkin, and Robinson (J., 1927, 3015) and this substance is certainly different from iretol monomethyl ether. We have not, however, been able to satisfy ourselves that the phenol (VIII) is identical with the iretol derivative, and this matter requires further investigation; the present position is explained in the experimental section.

An application of the Hoesch reaction, using methoxyacetonitrile (compare Slater and Stephen, J., 1920, **117**, 309), led to the formation of a *trimethoxyresacetophenone* (IX) and the veratroylation of this ketone gave a *hydroxypentamethoxyflavone* (X). The hexahydroxyflavone obtained on demethylation in the usual manner was proved to be identical with gossypetin (II). The various stages of this synthesis can proceed in one direction only and consequently the structure of the final product is established. For example, the oxidation product of tribenzyloxybenzene might have been 2 : 3-dibenzyloxy-*p*-benzoquinone; this, however, is definitely excluded by the success of the flavone synthesis, which proves that there is a hydroxyl group in the *o*-position to carbonyl in the dihydroxytrimethoxyacetophenone of the series. In contrast with quercetagetin pentamethyl ether (XI) (see below) the substance (X) is readily soluble in aqueous alkalis and exhibits a very weak ferric chloride reaction.

The synthesis of quercetagetin proceeds from 4 : 5-dimethoxyresorcinol (XII) by a similar series of reactions and since the final

product, a hexahydroxyflavone, is different from gossypetin it must have the *constitution* (III), the only alternative to (II) under the conditions. This substance proved to be identical with quercetagetin.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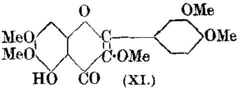
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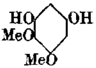
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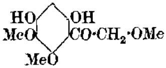
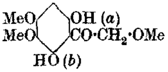

(XIII.)


(XIV.)

The preparation of a dihydroxytrimethoxyacetophenone from 4 : 5-dimethoxyresorcinol and methoxyacetonitrile was carried out by Chapman, Perkin, and Robinson (*loc. cit.*) and the formula (XIII) was attributed to the ketone on grounds of analogy. Had this view been correct, the hydroxypentamethoxyflavone derived from the substance by veratroylation would have been a 7-hydroxyflavone. The product actually obtained had, however, the characteristics of a 5-hydroxyflavone; it gave a ferric chloride reaction and the phenolic function was very feebly exhibited. The properties of the substance were indeed identical with those of Perkin's quercetagetin pentamethyl ether (*loc. cit.*) obtained by the methylation of quercetagetin and it is well known that it is the hydroxyl in position 5 that *offers the greatest resistance to methylating agents.* These considerations prove that the methoxyacetyl derivative of 4 : 5-dimethoxyresorcinol *has the constitution* (XIV) *and the orientation* phenomenon thus brought to light is a very interesting one. The pyrone ring formed in the course of the veratroylation of (XIV) might be closed in the direction (*a*) or (*b*) in the formula; but it is evidently the hydroxyl (*a*) that is involved, because otherwise the flavonol obtained on demethylation would be gossypetin. This is in agreement with Bargellini's view of the direction of ring-closure occurring in his syntheses of baicalein and scutellarein (*Gazzetta* 1915, **45**, *i*, 69; 1919, **49**, *ii*, 47), where the alternatives are analogous, the orientation of groups in the benzene nucleus being identical in all the cases under consideration.

We are greatly indebted to Professor A. G. Perkin, F.R.S., who has kindly sent us specimens of hexa-acetylgossypetin, gossypetin and quercetagetin which have rendered possible a comparison of the natural and the synthetic products. All the analyses recorded

were carried out by micro-methods, the majority of them by Dr. Ing. A. Schoeller of Berlin-Schmargendorf; substances with many methoxyl groups were burned slowly at a specially high temperature.

EXPERIMENTAL.

1 : 2 : 3-*Tribenzyloxybenzene* (IV).—The following are the best conditions yet found for the benzylation of pyrogallol. A mixture of pyrogallol (50 g.), anhydrous potassium carbonate (240 g.), and dry acetone (300 c.c.) was refluxed in an atmosphere of hydrogen for 30 hours, benzyl chloride (210 g.) being gradually introduced; the mixture was then kept under the same conditions for a further 10 hours. The portion of the reaction product that was insoluble in water was dissolved in ether and washed with aqueous sodium hydroxide, and the solvent and unchanged benzyl chloride were removed by distillation, finally in steam. The residue was crystallised from alcohol (yield, 50 g.) and on recrystallisation the substance was obtained in colourless needles, m. p. 70° (Found: C, 82·4; H, 6·2. $C_{27}H_{24}O_3$ requires C, 81·8; H, 6·0%). It is readily soluble in benzene, ether, acetone, and chloroform and is moderately readily soluble in alcohol, light petroleum, and acetic acid.

2 : 6-*Dibenzyloxy*-p-*benzoquinone* (V).—Nitric acid (40 c.c.; *d* 1·19) was added to a solution of 1 : 2 : 3-tribenzyloxybenzene (80 g.) in acetic acid (800 c.c.) at 40°. After the mixture had been kept for 4 hours at room temperature, the liquid was filtered; the solid residue (15 g.), which consisted chiefly of 5-*nitro*-1 : 2 : 3-*tribenzyloxybenzene* (oriented by analogy only), crystallised from acetone in long colourless needles, m. p. 139° (Found: N, 3·2. $C_{29}H_{23}O_5N$ requires N, 3·2%). A second quantity of nitric acid (40 c.c.; *d* 1·19) was added to the reddish-brown filtrate and on the following day the *quinone* that had separated was isolated (30 g.); addition of much water precipitated a further small quantity of the same substance. This crystallised from acetone in long yellow needles, m. p. 201—202° (Found: C, 75·0; H, 5·3. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%), sparingly soluble in most organic solvents but readily solnble in chloroform.

2 : 6-*Dibenzyloxyquinol* (VI).—Sulphuric acid (60 c.c. of 25%) was gradually added during 3 hours to a gently boiling, well-stirred mixture of dibenzyloxybenzoquinone (40 g.), alcohol (400 c.c.), and zinc dust (80 g.). When the yellow quinone had disappeared, the liquid was filtered hot. Addition of dilute sulphurous acid to the filtrate caused the separation of lustrous pearly-white plates (40 g.). The *quinol*, after recrystallisation by the addition of aqueous sulphurous acid to an alcoholic solution, had m. p. 116—117°

(Found : C, 74·5; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). It is readily soluble in alcohol, acetone, ether, and chloroform, moderately readily soluble in hot water, and sparingly soluble in benzene, light petroleum, and cold water.

Reoxidation to the quinone occurs readily in the presence of moisture and is accelerated by alkalis; the crystals develop a fine green coloration in contact with concentrated aqueous potassium hydroxide. Ferric chloride oxidises the quinol very rapidly and smoothly with formation of the quinone.

2 : 6-Dibenzyloxy-1 : 4-dimethoxybenzene (VII).—Aqueous sodium hydroxide (12 g. of a solution of 60 g. of sodium hydroxide in 150 c.c. of water) and then methyl sulphate (16 g.) were added to a vigorously agitated mixture of 2 : 6-dibenzyloxyquinol (12 g.) and alcohol (120 c.c. of 90%) contained in a vessel from which air was excluded by hydrogen. A further quantity (7 g.) of the sodium hydroxide solution was introduced in the course of 9 hours in order to keep the solution weakly alkaline; the temperature was then raised to about 45° for 1 hour and, after 12 hours, water (50 c.c.) was added and the deposited crystals were collected (12 g.). The substance separated from acetone in massive colourless crystals, m. p. 82—83° (Found : C, 75·5; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%). It is readily soluble in most organic solvents but is sparingly soluble in cold alcohol and boiling light petroleum.

2 : 5-Dimethoxyresorcinol (VIII).—A mixture of 2 : 6-dibenzyloxy-1 : 4-dimethoxybenzene (10 g.), acetic acid (70 c.c.), and hydrochloric acid (30 c.c.; *d* 1·16) was kept at 65—70° for an hour. A large volume of water was then added, the solution was evaporated to a syrup under diminished pressure and extracted with hot water, and the extract was evaporated in a vacuum desiccator over sulphuric acid and sodium hydroxide. Brownish-yellow prisms (3 g.) separated; at the same time a small amount of a different crystalline substance, m. p. 180°, was deposited, but this was not further examined. The main product crystallised from water in faintly brownish-yellow prisms, m. p. 61—62°, and would doubtless be colourless when pure (Found in air-dried material : C, 46·8; H, 6·9; MeO, 29·1; loss at 56° in a high vacuum, 17·7. $C_8H_{10}O_4,2H_2O$ requires C, 46·6; H, 6·9; 2MeO, 30·1; $2H_2O$, 17·5%). 2 : 5-*Dimethoxyresorcinol* is moderately readily soluble in cold water and is readily soluble in most organic solvents; it imparts a purple colour to a pine shaving moistened with concentrated hydrochloric acid. The material dried at 56° in a vacuum had m. p. 86—88°; the hydrated specimen crystallised from benzene unchanged (m. p. 61—62°), but the anhydrous one, on solution in hot benzene and cooling, gave crystals, m. p. 182°. These gave no ferric chloride

reaction, whereas an aqueous solution of the crystals of m. p. 61—62° developed a weak bluish-violet coloration on the addition of ferric chloride.

The benzene mother-liquor from the crystals of m. p. 182° was concentrated to a syrup and on the addition of a little water this gave prisms, m. p. 61—62°.

Iretol monomethyl ether is stated to crystallise from benzene in an anhydrous form, m. p. 87° (de Laire and Tiemann, *loc. cit.*), and to give a deep blue coloration with ferric chloride.

The question of the constitution of this phenol remains an open one and further investigations are in progress.

2 : 4-*Dihydroxy*-ω : 3 : 6-*trimethoxyacetophenone* (IX).—A solution of anhydrous 2 : 5-dimethoxyresorcinol (3·1 g.) and methoxyacetonitrile (2·0 g.) in dry ether (30 c.c.) was saturated with hydrogen chloride and kept over-night at room temperature. The ketimine hydrochloride formed a faintly yellow crust and a further quantity was precipitated in a semi-solid condition on the addition of dry ether. The salt was washed with ether and dissolved in water (50 c.c.), and the solution heated on the steam-bath for 1 hour. On cooling, the crude *ketone* crystallised readily (yield, 3·6 g.); it separated from hot water in long colourless needles, m. p. 150—151° (Found: C, 54·7; H, 6·0; MeO, 38·3. $C_{11}H_{14}O_6$ requires C, 54·5; H, 5·8; 3MeO, 38·4%). Alcoholic ferric chloride produced an intense bluish-brown coloration.

7-*Hydroxy*-3 : 5 : 8 : 3′ : 4′-*pentamethoxyflavone* (O-*Pentamethylgossypetin*) (X).—A mixture of 2 : 4-dihydroxy-ω : 3 : 6-trimethoxyacetophenone (2 g.), potassium veratrate (7 g.), and veratric anhydride (20 g.) was heated (oil-bath at 175—180°) for 4—5 hours, and the melt dissolved in boiling alcohol (150 c.c.). Hydrolysis was effected by means of potassium hydroxide (6·5 g.) dissolved in water (15 c.c.), which was gradually added during 20 minutes to the boiling liquid. The alcohol was removed by distillation under diminished pressure and the residue was dissolved in water and saturated with carbon dioxide; very little of the flavonol was precipitated. The filtrate from this small amount was acidified with hydrochloric acid, the veratric acid that separated was rapidly collected, and the filtrate kept for some hours. Woolly needles were deposited, and more of the same substance was obtained from the mother-liquor after concentration under diminished pressure. The substance, after precipitation from very dilute potassium hydroxide solution by means of carbon dioxide and keeping for a few hours (yield, 0·7 g.), crystallised from aqueous acetic acid in long faintly greenish-yellow needles, m. p. 250—253°, and was then sufficiently pure for most purposes. On recrystallisation from aqueous alcohol, yellow

needles, m. p. 253—254°, were obtained (Found in material dried at 120°: C, 61·9; H, 5·4; MeO, 39·1. $C_{20}H_{20}O_8$ requires C, 61·8; H, 5·2; 5MeO, 40·0%).

The flavonol derivative dissolves in concentrated hydrochloric acid and in aqueous alkalis to yellow solutions; it develops no characteristic coloration with ferric chloride in alcoholic solution.

3 : 5 : 7 : 8 : 3′ : 4′-*Hexahydroxyflavone* (*Gossypetin*) (II).—The foregoing pentamethyl ether was boiled with an excess of hydriodic acid (*d* 1·7) for 35 minutes. On addition of dilute sulphurous acid a yellow solid separated, which crystallised from aqueous alcohol in yellow microscopic needles, m. p. 310—314° (difficult to observe owing to decomposition and blackening of the tube) (Found in material dried at 150°: C, 56·3; H, 3·6. Calc. for $C_{15}H_{10}O_8$ C, 56·6; H, 3·2%).

The substance is readily soluble in cold alcohol and very sparingly soluble in water and gives a bright yellow solution in sulphuric acid. In these respects and also in its behaviour towards ferric chloride and lead acetate in alcoholic solution, the synthetical material agrees exactly with gossypetin (m. p. 311—313°). A specimen of the hexa-acetyl derivative of gossypetin kindly provided by Professor A. G. Perkin was hydrolysed for a comparison of the highly characteristic reactions in alkaline solutions.* When very small quantities were employed it was difficult to reproduce the recorded colour changes because it was hard to avoid the use of too much alkali and the reaction was too rapid. The most trustworthy procedure involved the use of buffered solutions and we have employed those prepared from the "Universal Buffer Mixture" supplied by the British Drug Houses Limited. The natural and the synthetic specimen exhibited an identical behaviour. The flavonol is not dissolved by the solution of p_H 6·2 nor by that of p_H 6·8, but in the latter case reaction proceeds slowly and the solid gradually disappears, the solution becoming pale reddish-brown. Gossypetin dissolves in a solution of p_H 8·0 and the yellow solution slowly changes through brownish-green, brownish-purple and grey-purple to a weak grey; it never exhibits a blue colour.

Oxidation is more rapid in more alkaline solutions and at p_H 8·(the more characteristic changes become apparent. The most convenient reagent is, however, that of p_H 9·8; this dissolves the flavonol to a yellow solution, and on agitation with air the colour changes to green and then to a fine pure blue, the latter being relatively stable. The further change to brown (and finally loss of colour intensity) is very slow but is more rapid in the more alkaline

* Subsequently the reactions of a different specimen of natural gossypetin were observed with the same results.

solutions; at p_H 11·0 the yellow solution very quickly becomes green and blue and the intensity rapidly diminishes, the liquid becoming slate-blue, grey, and finally almost colourless. When the blue solutions are acidified they become red. The preparation of gossypetone by oxidation of the synthetic gossypetin with *p*-benzoquinone in alcoholic solution was also carried out on a very small scale; the substance separated in the way described by Perkin (*loc. cit.*) and had the recorded appearance and properties.

O-*Hexa-acetyl Derivatives*.—The synthetic gossypetin was acetylated by means of boiling acetic anhydride and a drop of pyridine during 2 hours; the product was isolated and treated again in the same way. The substance then crystallised from alcohol in sparingly soluble, colourless needles; these melted at 229—230°, and at the same temperature when mixed with a specimen of *O*-hexa-acetylgossypetin obtained by re-acetylation and crystallisation of the material of natural origin.

3 : 5 : 7 : 8 : 3′ : 4′-*Hexamethoxyflavone* (O-*Hexamethylgossypetin*).—The hydroxypentamethoxyflavone described above was methylated by means of potassium hydroxide and methyl sulphate in aqueous-alcoholic solution; the derivative crystallised from alcohol in glistening colourless needles, m. p. 170—172° (as stated by Perkin for *O*-hexamethylgossypetin) (Found: C, 62·5; H, 5·7. Calc. for $C_{21}H_{22}O_8$: C, 62·7; H, 5·5%). In this case two analyses by ordinary methods gave low values for carbon. The substance dissolves in concentrated hydrochloric acid to an intensely yellow solution; the colour is partly discharged on addition of water and wholly when, on keeping, the substance separates in very long, slender, colourless needles.

2 : 6-*Dihydroxy*-ω : 3 : 4-*trimethoxyacetophenone* (XIV).—This was prepared essentially as described by Chapman, Perkin, and Robinson (J., 1927, 3015); the ketimine was best precipitated by the addition of 100 c.c. of a mixture of equal volumes of ether and ligroin, and was hydrolysed by heating with water (20 c.c.) and concentrated hydrochloric acid (2 c.c.) on the steam-bath for 2 hours. After treatment with charcoal and filtration, the ketone separated on cooling.

5-*Hydroxy*-3 : 6 : 7 : 3′ : 4′-*pentamethoxyflavone* (O-*Pentamethylquercetagetin*) (XI).—A mixture of the above ketone (1·0 g.), veratric anhydride (15 g.), and sodium veratrate (6 g.) was heated at 180—190° for 8 hours. The resulting resin was warmed with much dilute sodium carbonate solution, and the collected product was dissolved in hot alcohol (100 c.c.) and hydrolysed by boiling for 15 minutes with potassium hydroxide (6 g.) dissolved in a little water. The solution, when diluted with water (100 c.c.) and saturated with

carbon dioxide, deposited yellow crystals; the separation was completed by the further addition of water (400 c.c.). Crystallisation from alcohol (charcoal) gave thin, lustrous, pale yellow needles (1 g.), m. p. 158—159°. Further crystallisation from methyl alcohol raised the melting point to 159—160° (Found: C, 62·0; H, 5·3. $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2%). This *O-pentamethylquercetagetin* is almost insoluble in cold, aqueous alkaline solutions, but dissolves on warming or on the addition of a little alcohol. Its solution in alcohol develops a brownish colour with a trace of ferric chloride and an intense, dull olive-green with an excess. In concentrated sulphuric acid it gives an intensely yellow solution, which becomes cherry-red on addition of a trace of nitric acid.

O-Hexamethylquercetagetin.—*O*-Pentamethylquercetagetin (0·3 g.) was methylated in acetone solution at about 60° by shaking with aqueous sodium hydroxide and methyl sulphate. The initial bright yellow colour faded, and the alkaline solution was then heated for a short time on the steam-bath. Addition of water caused the separation of colourless needles, which were washed and crystallised from 50% alcohol. The lustrous prismatic needles (0·3 g.) obtained consisted of the α-form, m. p. 141—143°. On crystallisation from acetone, larger, somewhat irregular prisms of the pure α-form were deposited, m. p. 143—144° (Found: C, 62·7; H, 5·5. Calc. for $C_{21}H_{22}O_8$: C, 62·7; H, 5·5%). This specimen again crystallised from acetone in the α form. A different specimen, however, separated at once from acetone in tiny, thick, rhomboidal prisms (hexagonal in outline when crystallised very slowly) of the β-form, m. p. 157°. The molten α-form at about 145°, when seeded with the solid β-form, at once solidified to a mass of the β-form, m. p. 157°. The melting point of an intimate mixture of the two forms was also 157°. *O*-Hexamethylquercetagetin dissolves in concentrated hydrochloric acid with production of an intensely yellow colour, which fades on dilution and disappears on neutralisation.

Dimorphic forms of *O*-hexamethylquercetagetin of the same melting points have been described by A. G. Perkin (*loc. cit.*) in the case of the ether prepared from natural quercetagetin, and the recurrence of these observations in the case of our synthetic specimens affords very strong evidence that the natural and the synthetic product are indeed identical.

There is a theoretical possibility that some gossypetin derivative might accompany the synthetic quercetagetin methyl ethers. The following observation suggests that this may be so.

The methylation of a specimen of *O*-pentamethylquercetagetin obtained by working up its alcoholic mother-liquors gave the hexamethyl ether as very fine needles from acetone. After slight sinter-

ing, these gave a turbid, incompletely fluid melt at 157°, which cleared suddenly and became perfectly fluid at 170° (gossypetin hexamethyl ether has m. p. 170—172°). The small amount of material at our disposal did not allow us to follow up this interesting point.

3 : 5 : 6 : 7 : 3′ : 4′-*Hexahydroxyflavone* (*Quercetagetin*) (III).—When *O*-pentamethylquercetagetin (0·5 g.) was treated with freshly distilled hydriodic acid (5 c.c.; *d* 1·7), solution first took place and then orange crystals of a hydriodide separated. The mixture was heated for 1 hour at 140° (bright orange-red crystals of a hydriodide separating), water (100 c.c.) added, and the whole heated on the steam-bath for 15 minutes. The light yellow product was crystallised twice from 50% acetic acid (charcoal) and obtained in tiny, pale yellow, prismatic needles which melted when rapidly heated at about 316° with much decomposition and darkening (Found in material dried at 160°: C, 56·4; H, 3·2. Calc. for $C_{15}H_{10}O_8$: C, 56·6; H, 3·2%). When crystallised from 50% acetic acid, the substance contains water of crystallisation (Found: H_2O, 9·9. $C_{15}H_{10}O_8,2H_2O$ requires H_2O, 10·2%).

This synthetic quercetagetin was slightly soluble in boiling water, and the cooled air-free solution, treated with a drop of exceedingly dilute, air-free sodium hydroxide solution, became at first pure yellow, but, on shaking, rapidly turned bright olive-green and then deep yellowish-brown. With stronger alkali the green colour was not observed. The oxidation of quercetagetin in buffered alkaline solution is much less facile than that of gossypetin. At p_H 9·8 the yellow solution slowly becomes bright green, brown-green, and brown; at p_H 10·4 the same changes occur more rapidly; and a solution of p_H 11·0 is at first yellow, rapidly becomes green and then yellow-brown, duller brown, and brownish-red. A dilute alcoholic solution treated with ferric chloride gave an intense, dull olive-green coloration. The addition of an alcoholic solution of lead acetate threw down a bright orange-red precipitate which slowly became more yellow. A solution in alcohol treated with a drop of alcoholic potassium hydroxide gave a yellow precipitate which slowly (or quickly on the addition of more alkali) turned green and finally brownish-black, and the addition of a trace of sodium amalgam gave greenish flocks. This last reaction is characteristic of scutellarein, baicalein (Bargellini, *Gazzetta*, 1919, **49**, ii, 47) and irigenol (Baker, J., 1928, 1030), all of which contain hydroxyl groups in positions 5, 6, and 7.

The *hexa-acetyl* derivative was obtained by boiling the synthetic quercetagetin with acetic anhydride and a few drops of pyridine for 1½ hours. It slowly separated from the filtered solution after the addition of alcohol, and crystallised from acetic acid–alcohol in

bunches of colourless needles, m. p. 210° with slight previous softening (Found : C, 56·8 ; H, 3·8. $C_{27}H_{22}O_{14}$ requires C, 56·9 ; H, 3·8%).

A specimen of the derivative similarly prepared from quercetagetin of natural origin also melted at 210° with slight previous softening, and a mixture of the synthetic and the natural specimen had exactly the same softening and melting point.

Dyeing Properties of the Flavonols.—The behaviour of the synthetic and the natural specimens of gossypetin (that obtained from the acetate and also a second larger specimen of the flavonol itself, kindly supplied by Professor A. G. Perkin) and of quercetagetin towards alkaline solutions and in other respects was found to be *identical by direct comparison, but, doubtless owing to a difference* in the conditions employed, we thought there was some divergence between the results of our dye-trials with synthetical quercetagetin and the shades recorded by Perkin (*loc. cit.*). A direct comparison showed that no variations actually exist. The shade on tin-*mordanted* wool was brownish-orange and on chromium-mordanted wool dull yellowish-greenish-brown.

The colours on calico mordanted with iron and aluminium were the following, natural and synthetic specimens giving identical results :

	Weak Al.	Strong Al.	Al + Fe.	Strong Fe.	Weak Fe.
Gossypetin ...	Brownish-grey	Khaki-brown	Dull greenish-brownish-grey	Smoke-brown	Mouse-grey
Quercetagetin	Greenish-yellow	Deep brownish-yellow	Greenish-brown	Intense bluish-black	Greenish-grey

1 : 2 : 3 : 5-*Tetramethoxybenzene.*—When this work was completed it occurred to us that a valuable confirmation of the view that gossypetin and quercetagetin are derivatives of the same tetrahydroxybenzene could be obtained by equating the starting points of the syntheses. Accordingly 2 : 5-dimethoxyresorcinol and 4 : 5-dimethoxyresorcinol were separately methylated by means of methyl sulphate and sodium hydroxide in aqueous acetone solution. The products were isolated in the usual manner and vacuum-distilled from very small flasks. The ether from 2 : 5-dimethoxyresorcinol, which was prepared first, solidified when rubbed. The small quantity of the ether produced from 4 : 5-dimethoxyresorcinol remained liquid, but crystallised immediately when a crystal of the ether prepared from 2 : 5-dimethoxyresorcinol was introduced. A mixture of the two specimens and that from 2 : 5-dimethoxyresorcinol separately exhibited an identical behaviour on fusion and solidification; the m. p. was 45—46° (Will, *Ber.*, 1888, **21**, 609, gives 47°).

THE UNIVERSITIES OF OXFORD AND MANCHESTER.
UNIVERSITY COLLEGE, LONDON. [*Received, November 9th, 1928.*]

XV.—*The Electrical Behaviour of Surfaces of Corroding Iron.*

By A. L. McAulay and S. H. Bastow.

The corrosion of iron is usually the result of electrochemical action caused by the passage of currents between portions of the metal which are at different potentials with respect to an electrolyte in contact with them. The differences of potential are produced by differential aeration (Evans, "Corrosion of Metals," Chap. VI), but the conditions under which they are produced generally depend on such a variety of factors that it has not been possible to obtain much information as to the mechanism of their production and behaviour, and this lack of knowledge necessarily limits our control of the phenomenon.

The present investigation was initiated with a view to elucidate the mechanism giving rise to corrosion currents, but it immediately became evident that an important part of the work must be the attainment and recognition of a standard condition for metal and solution. It was found that two apparently identical pieces of electrolytic iron, cut from the same sheet and having similarly ground surfaces, gave widely different potentials on immersion in an electrolyte and had distinctly different subsequent histories. This point is illustrated by Curves 1 and 2, Fig. 2, in which the potential of an electrode immersed in an electrolyte is plotted against time of immersion.

As a result of our work, we reach the following conclusions. When a piece of iron is placed in an air-free electrolyte, there is a stable potential to which it tends, probably ultimately determined by the hydrogen-ion concentration of the solution. It does not immediately acquire this potential, but after prolonged immersion the stable condition, which proved to be easily reproducible, is attained, and the behaviour of the metal when subjected to experiments using this condition as a starting point is also reproducible.

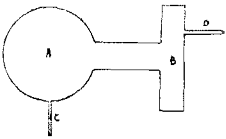
Curves 3, 4, 5, and 6 of Fig. 2 are of a similar type to 1 and 2, but relate to an electrode first brought into this standard state, the nature of which was found to be almost independent of the composition of the iron. Iron corroding in a neutral electrolyte not rendered air-free is in a stable condition which has most of the characteristics of that just described, although it depends to some extent on the degree of aeration of the electrolyte.

Experimental.

Apparatus.—The apparatus used (Fig. 1) consisted of a Pyrex-glass flask, A, and a tube, B, forming a T-piece with the neck; B

was the half-cell containing the iron electrode, and A served as a reservoir of air-free electrolyte. The apparatus was first placed with B above A and the solution was boiled for about ½ hour to free it from air. Towards the end of the boiling, oxygen-free nitrogen was admitted sparingly through the capillary tube, C. After the boiling, the side tube, D (which later served to make contact with the calomel electrode), was blocked with filter-paper, the apparatus was turned on its side, B and D were filled with solution, and the whole was maintained under a pressure of nitrogen of about one foot of water. The iron electrodes were inserted through rubber bungs into the ends of B. Two electrodes were sometimes used in order to carry out two experiments at the same time. It was found possible to make the changes from electrode-bearing bungs to plain bungs quickly and without contaminating the solution noticeably with oxygen (see below). The pressure applied gradually through C made it easy to get rid of any bubbles of air that might tend to lodge under the bungs. This cell was connected through D to a calomel electrode and the potentials of the electrodes were measured against it by a potentiometer in the usual way.

FIG. 1.



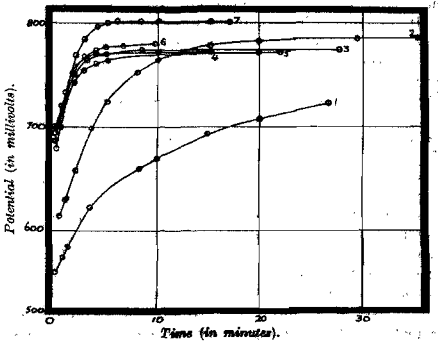
Earlier experiments with more complicated apparatus had shown (1) that it was possible to expose the surface of the air-free electrolyte for a few moments to air, as when changing bungs to make an exposure or insert an electrode, without producing contamination, and (2) that it was highly desirable to have the reservoir containing the air-free solution in direct communication with the cell without the intervention of rubber-tube connexions.

The Standard State.—Curves 3, 4, 5, and 6 of Fig. 2 are typical of a series of 20 obtained with several electrodes which had all been previously immersed for at least 12 hours in an air-free $N/2$-potassium sulphate solution and then exposed for 1 minute to air and replaced in the solution. All potentials are given against the saturated calomel electrode, but no corrections were made for liquid–liquid junction potentials, etc., so the values are not to be considered as absolute. Except where stated to the contrary, all the electrodes were made from a sheet of electrolytic iron kindly given to us by Mr. U. R. Evans, and having the following impurities: C, 0·04; Mn, 0·025; Si, 0·010; S, 0·013; P, 0·017; Ni, 0·09%; Cr, nil.

The similarity of these four curves and their wide difference

from curves 1 and 2 is striking. The last two curves represent the behaviour of electrodes from the same sheet of metal, ground with emery paper under the same conditions, and then immersed in air-free $N/2$-potassium sulphate. Curves 3 and 4 were given by the same electrode, but the surface had been reground between the two experiments; Curves 5 and 6 were obtained with separate electrodes. Different samples of electrolyte were used in each of these four cases. Curve 7 shows the result of similar treatment *when the condition of the solution is slightly altered. It is intended*

FIG. 2.



Curves 1 and 2 show the attainment by the electrode of the standard state after being polished with emery paper and immediately immersed in electrolyte. Curves 3, 4, 5, 6, 7 show recovery of electrode to standard condition after an exposure of 1 minute in each case. (All potentials are on the saturated calomel scale.)

to investigate further the cause of the different equilibrium potentials obtained with different solutions. The indications at present are that the completeness with which the solution is freed from oxygen partly determines these potentials, but it is also fairly certain that hydrogen-ion concentration exercises a marked effect. For solutions thoroughly boiled and left standing in contact with iron for 12 hours or more, the extreme variation observed is about that shown by the gap between Curves 3, 4, 5, and 6 and Curve 7. It will be noticed that the general form of all five curves is the same.

The condition to which the electrodes used in these and similar experiments have attained was taken as a standard. It could always

be achieved by the immersion for many hours of an electrode in an air-free electrolyte. No other treatment gave such reproducible surface conditions, although qualitative reproducibility could be obtained with electrodes which had been immersed for a long time in an electrolyte not rendered air-free. Here the potential reached was not so base as in the standard state, and the time required to regain that potential after exposure to air was greatly increased.

The standard state is a direct result of action by the electrolyte and is not a spontaneous disappearance of the air-formed modification of the iron. This was tested by keeping the electrode for about ½ hour in oxygen-free nitrogen after a minute's exposure to air. Its subsequent behaviour was exactly the same as that of one of which the only treatment was a minute's exposure to air.

The interpretation of the above facts is as follows. The well-known and very variable electric condition of iron surfaces is due to the formation of a surface film of oxide, which is more or less cracked and remains in a state of continuous cracking and repair for a long time after the grinding of the surface (see Evans, J., 1927, 1020). This is probably further complicated by a greater or less adsorption of gas and other impurities in the surface. On immersion in an electrolyte such as potassium sulphate, the oxide film is gradually undermined and broken up, and any adsorbed material is removed, so that after the lapse of several hours the surface behaves electrically as a clean iron surface. In order that this should be the case, the film is not necessarily destroyed, for it is possible to achieve the standard state with a visible and apparently adherent coat of yellow oxide covering the electrode, and the subsequent electrical history of such an electrode on exposure to air and re-immersion is the same as that of one which is bright. This is demonstrated by Curve 6, Fig. 2, which was obtained with an electrode brought into the standard state after a previous treatment of alternate oxidation and reduction: it was covered with a visible yellow film on which were large grey patches.

The Effect of Oxidation on Iron in the Standard State.—A series of experiments was made with iron electrodes, brought to the standard state and then exposed to air for a few seconds, 1 minute, 5, 10, 30, 45, 120, 250, or 1125 minutes. The "effect" was measured by the changes of potential with time on immersion of the electrode, after exposure, in air-free electrolyte. In the shortest exposure, the electrode was taken wet from the solution and immediately returned to it, so that any slight amount of air which did reach it had to diffuse through a layer of solution and the effective exposure was probably extremely short. Even this exposure made the iron sensibly more noble, and the potential only returned to its original

value after 2 or 3 minutes; presumably this represents the time needed for the destruction of the film by the electrolyte. Longer exposures resulted in a greater change of the potential and greater resistance of the film to subsequent destruction.

The curves obtained showed (i) that the potential immediately after immersion measures in some sense the state of the iron surface at immersion, and (ii) that the time required for the restoration of the normal state measures the resistance of the film to destruction.

After about 2 hours' exposure to air the change in condition of the surface produced by further exposure is small as measured by the time taken to recover the standard state. The obvious conclusion is that the film in this time has reached a state in which it protects the metal beneath from further action. It appears, however, as though the outside layer of the protective film were still undergoing modification.

The curves obtained after exposure to a powerful oxidising agent such as potassium chromate or anodic treatment in sodium hydroxide solution indicated the existence of a film which is more resistant to attack by electrolyte than that given by the longest air exposure. Prolonged immersion in air-free electrolyte restored the electrode to the standard state, although the restoration was much slower.

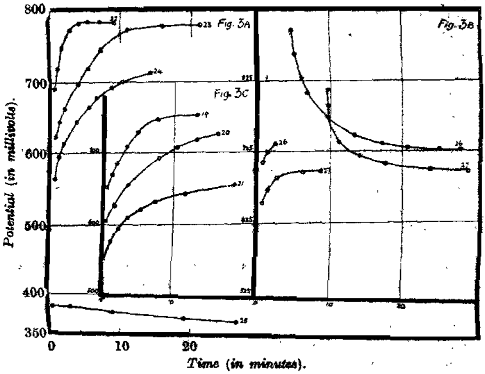
As the currents responsible for the corrosion of iron immersed in a normally aerated electrolyte are due to potential differences produced similarly to those described above, it might be thought probable that their passage would destroy the film producing these potential differences, the energy for the current coming from the cathodic reduction of the oxide. The following experiments were made with a view to test this.

The Effect of the Passage of Current on the Destruction of the Ennobling Film on Iron.—When an electrode is immersed in electrolyte after exposure to air, the passage of currents of density about 40 microamps. per sq. cm. to the electrode as cathode seems to have no effect on the form of the time-potential curve, beyond a temporary polarisation. Two electrodes were exposed to air for 10 minutes prior to making the experiment; in one case, no current was passed, but in the other, 3 minutes after immersion, 40 microamps. per sq. cm. were passed to the iron as cathode for 1 minute. The polarisation effect was found to disappear after about 1 minute. This can only be interpreted as meaning that the air-formed modification of the iron is unaffected by the passage of corrosion currents. Anodic treatment (40 microamps. for 1 minute) was found to have scarcely any effect at all on the electric condition of the surface.

Experiments on Cast Iron, Mild Steel, and "Stainless" Steel.—Experiments with cast iron and mild steel indicate that their

general behaviour is very similar to that of electrolytic iron. The curves for corresponding exposures, though not of exactly the same form, follow the general lines of those obtained with electrolytic iron. *Fig.* 3C shows curves for exposures of 1, 5, and 54 minutes on mild steel (19, 20, 21), and Fig. 3A those of 1, 10, and 100 minutes on cast iron (22, 23, 24). The electrodes come to a standard state after prolonged immersion in electrolyte, but in this state they are

FIG. 3.



(A) *Curves 22, 23, and 24 show recovery of cast-iron electrode to the standard condition after exposure to air of 1, 10, and 100 minutes. Curve 25 shows effect of a 5-minute exposure to air on a stainless steel electrode.*

(B) *Curves 26 and 27 show effect of passing a current of 40 microamps. for 1 minute on electrodes of mild steel and cast iron.*

(C) *Curves 19, 20, and 21 show recovery of mild-steel electrode to the standard condition after exposure to air of 1, 5, and 54 minutes.*

much more sensitive and go out of the standard state much more easily.

Experiments with current indicate that cast iron and mild steel are more easily polarised, the polarisation effect being large compared with that of pure iron. This renders the task of finding the to fect of passage of current upon the passifying film more difficult. diffusindications are that it is unaltered. Curves 26 and 27, Fig. 3B, probab the effect of passing a current of density about 40 microamps. sensibly am. for 1 minute to electrodes of mild steel and cast iron,

"Stainless" steel, as was anticipated, gave a completely different result—Curve 25, Fig. 3A, shows its behaviour when given an exposure to air of 5 minutes. After immersion in the electrolyte for 12 hours it was still in the same condition as when first put in. It behaved like a noble metal in having no definite potential of its own in the solution and in being extremely easily polarised so as to take up almost any potential.

Summary.

Iron when corroding is in a stable and reproducible state, and, provided that the electrodes are first aged by prolonged immersion in an electrolyte and the condition of aeration of the electrolyte is standardised, reproducible results can be obtained.

The behaviour of pure electrolytic iron is also typical of that of mild steel and cast iron; difference in composition has but little effect provided that it is not such as to produce air passivity, as in the case of "stainless" steel. Such steel shows completely different behaviour: it resembles a noble metal, is easily polarised by minute currents, and shows no very definite normal potential.

The potential which an iron electrode reached after prolonged immersion in an air-free electrolyte was taken as standard. In $N/2$-potassium sulphate this is between 0·75 and 0·80 volt on the saturated calomel scale, the actual value probably depending on the p_H of the solution. Electrodes in this condition were given various exposures to air and re-immersed in the same electrolyte; the resulting potentials were measured, and their change with time observed. The curves showing this change with time, *i.e.*, the rate of recovery of the standard state, demonstrate that the film which is responsible for the corrosion current increases in protective power and resistance to destruction with time of exposure of the iron to air up to about 2 hours, after which but little further change takes place on further exposure.

When this stage is reached immersion of the iron in air-free $N/2$-potassium sulphate causes a destruction of the ennobling film in about an hour, and a consequent return of the metal to the standard state in this time. Some film is formed even in the shortest exposures it was possible to give. The destruction of the film is due to action by the electrolyte; it is not destroyed if the electrode is merely left in contact with an inert gas after exposure.

More drastic oxidation, such as anodic treatment in alkali, produces a film which takes considerably longer to destroy on exposure to electrolyte than any that are air-formed; eventually, however, the same standard state is achieved in each case.

The passage of corrosion currents has no effect on the ennobling

film that gives rise to the potential differences which produce them. The potentials are modified temporarily owing to polarisation effects, but these effects rapidly disappear when the current is stopped, leaving the film unchanged except for the action of the electrolyte.

In conclusion, we wish to express our gratitude to Mr. U. R. Evans, without whose interest and encouragement this work would probably not have been carried out. We are particularly indebted to him for corresponding with us during the progress of the work, and so to some extent mitigating the disadvantages of distance from other laboratories where similar work is being carried out.

UNIVERSITY OF TASMANIA, HOBART. [*Received, October 30th, 1928.*]

XVI.—*The Passivity of Metals. Part II. The Breakdown of the Protective Film and the Origin of Corrosion Currents.*

By ULICK R. EVANS.

ONE of the difficulties affecting quantitative work on corrosion is that the attack is not uniform, but commences at a number of isolated points, the progress of the corrosion depending on the distribution of the points of origin. It is therefore important to decide how and why corrosion begins at such points. Two general views are held: (1) The points may be mouths of invisible *cavities in the metal*, the interiors of which, being less accessible to dissolved oxygen, should be anodic towards the area outside. (2) They may be merely *breaks in a protective film*, where the exposed metal will be anodic towards the surrounding film-covered surface.

Tammann and Bredemeier (*Z. anorg. Chem.*, 1925, **142**, 54) have shown that cavities are often present in apparently sound metal, and the work of Seligman and Williams (*J. Inst. Metals*, 1920, **23**, 159) has indicated that certain types of local corrosion are connected with such cavities in aluminium, but this is probably an exceptional case. Callendar (*Proc. Roy. Soc.*, 1927, *A*, **115**, 349), who has studied the corrosion of aluminium in detail, considers that "the primary cathode and anode areas on a pure metal are determined largely by the distribution of oxide and other films." Similarly, for brass, Bengough and May (*J. Inst. Metals*, 1924, **32**, 155, 228) record certain cases of local attack connected with pre-existing cracks or pores; but here again these examples are considered to be exceptional, and the investigators expressly

dissociate themselves from the views of Maass and Liebreich (*Z. Metallkunde*, 1923, **15**, 245), who consider that the grooves left on drawing brass are commonly responsible for serious corrosion. Bengough and his colleagues have long held the view that local failure of a protective "scale" is a frequent cause of localised attack (see, *e.g.*, Bengough and Hudson, *J. Inst. Metals*, 1919, **21**, 37).

On the other hand, the author and others have found some difficulty in regarding the sites of local corrosion simply as breaks in an otherwise continuous scale, since corrosion commences locally even on specimens carefully cleaned by abrasion. However, recent work has indicated that simple exposure to air causes a film to form over a metallic surface with astonishing rapidity (J., 1927, 1029), and thus the above objection has largely been removed.

The present work was designed to distinguish definitely between these two views and to apply the results to the study of the mechanism of corrosion.

EXPERIMENTAL.

Materials and Method.—Two samples of vacuum-melted electrolytic iron foil (E 26 and E 28) and two of mild steel (H 26 and H 28) were prepared specially through the kindness of Dr. W. H. Hatfield. The analyses of these samples were :

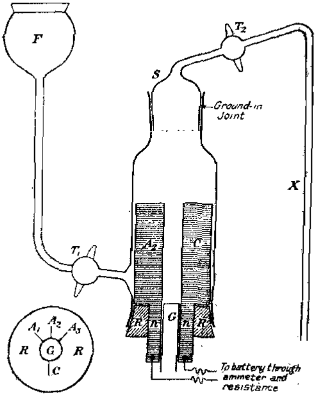
	E 26.	E 28.	H 26.	H 28.
Carbon	0·04	0·03	0·18	0·26
Manganese	0·025	0·04	0·56	0·57
Silicon	0·010	Trace	0·04	0·15
Sulphur	0·013	0·005	0·047	0·014
Phosphorus	0·017	0·020	0·028	0·018
Nickel and Copper	0·09	Nil	0·10	0·09
Chromium	Nil	Nil	Nil	Nil
Heat-treatment after rolling	Annealed above A_3	None	Annealed above A_3	None
Structure	Nearly equiaxial	Lamellar	Normal	Lamellar
Thickness, mm.	0·09	0·21	0·11	0·21

In addition, some specimens of sand-blasted steel were kindly supplied by Mr. W. E. Ballard. Two kinds of zinc were employed, one a commercial sheet zinc containing 1·29% of lead, and the other rolled, through the kindness of Mr. H. C. Lancaster, from electrolytic spelter of 99·97% purity. The copper was Kahlbaum's electrolytic foil; and of the two specimens of aluminium employed, one was a hard-rolled sheet with 0·34% Si and 0·39% Fe and the other an annealed sheet with 0·33% Si and 0·40% Fe. Throughout this paper the terms "finely ground surface" refer to a surface ground with No. 1 (French) emery, and the description "rolled surface" denotes the surface as produced by the rolling-mill, the

specimens being washed with benzene and then with alcohol, but not abraded.

Anodic Corrosion under Anaerobic Conditions.—The "cavity theory" outlined above will account for local corrosion when dissolved oxygen is present. If the liquid contains no oxygen or oxidising agent, and the corrosion is produced by an externally applied *E.M.F.*, there is no reason why the interior of cavities, as such, should be corroded more readily than other places, provided that the conditions are such that the corrosion is favoured by increase of current density.

FIG. 1.



The electrolysis vessel (Fig. 1) could be completely filled with liquid without air space. Since it was essential to introduce the electrodes without heating, the following arrangement was adopted. The rubber stopper, *R*, was pierced by a central round hole, from which four slits extended radially. The narrow portion (*n*) of each electrode was introduced into the central hole, and pushed sideways into its proper slit, which was held open by suitable pressure upon the rubber in a vice; when all four electrodes were in their four slits, a closed glass tube *G* was pushed into the central hole, and the outside smeared with Durofix, making a water-tight joint. The rubber stopper was then put into its place in the vessel and

the ground-in stopper S with side tube X was introduced. $M/10$-Potassium chloride was admitted through funnel F and tap T_1, the vessel being tilted to ensure that air was expelled through tap T_2, none being entrapped at S. When electrolysis was proceeding, T_2 was closed and T_1 slightly open, so that the hydrogen collecting at S could expel a corresponding portion of liquid. Three of the electrodes served as anodes and one as cathode. The anodes were prepared at least 24 hours before the experiment and kept in a desiccator.

Electrolysis was first conducted between the cathode and the central anode, which was always of iron, but no account was taken of the results of the corrosion of that anode, since the liquid still contained a little oxygen during this preliminary electrolysis. The precipitate formed by interaction between the cathodic and anodic products was at first brown, then green, and finally white. As soon as a considerable quantity of the white product (ferrous hydroxide) had accumulated, showing that no free oxygen remained, the second anode was connected in place of the first. When this showed signs of corrosion, the connexions were transferred to the third anode, which received a rather longer treatment. The anodes were then taken out and studied under the microscope.

Anodes of electrolytic iron, steel, aluminium (two varieties), and zinc (two varieties) were thus studied under different surface conditions; the mean current density employed in most of the experiments was 0·03 amp./sq. cm. In every instance, corrosion commenced locally at isolated points. On electrolytic iron, it remained local, producing neat little undercut cavities of which the diameter increased only slowly as corrosion proceeded. On zinc the attack spread out rapidly from the points of origin, and aluminium showed an intermediate behaviour. On steel the attack remained less localised than on pure iron. The position of the points of local corrosion is significant. On ground specimens the points occurred arranged on the deeper grooves, whereas on rolled specimens they either fell on lines indicating the rolling direction or were connected with surface defects; in many cases there was a special tendency for the points of attack to lie near the edge of the specimen, where the metal had been stressed in cutting. In one sample of hard aluminium, rolled some years previously, pitting occurred along lines left by the rolling; some, at least, of the points of pitting represented the sites of tiny white dots which existed on the sheet when received; these dots apparently were due to incipient atmospheric corrosion which had failed to develop. Aluminium annealed after rolling showed numerous clean-cut pits, sporadically distributed and independent of the rolling marks; but there were also areas

showing general etching, and the boundaries of these areas tended to follow the rolling direction.

Now, those points which favour the initiation of corrosion when an external *E.M.F.* is applied under anaerobic conditions are just those which favour corrosion in the presence of dissolved oxygen when no external *E.M.F.* is applied. The cause must be the same in both cases. The first case cannot be explained by assuming a difference in oxygen concentration between the interior and the exterior of hypothetical cavities. Hence we are forced to conclude that the sites of local corrosion simply represent weak spots in the protective coating. They cannot, however, in all instances be actual *gaps* in the film such as would admit gaseous diffusion, since gaps of that character would have been healed through the exposure to air before the experiment—at least in some of the cases examined. But they may well represent weak spots where chlorine ions will pierce the skin in preference to other places under the directive influence of the externally applied *E.M.F.* Such weak spots might, for instance, be places of great surface irregularity, or regions where intense internal stresses left in the metal keep the oxide skin in a distended condition. In some instances weak spots undoubtedly coincided with cavities in the metal itself; but there appeared no reason to think that the existence of pores (as such) is a necessary condition for localised corrosion.

Corrosion (*without Applied* E.M.F.) *under Conditions of Differential Aeration.*—Strips of rolled steel or zinc were scratched with a file or diamond point and immediately partly immersed in *M*/10-potassium chloride or sulphate. Corrosion quickly set in along the scratch-lines, and extended downwards, this being the direction of lowest oxygen concentration. Possibly gravity also facilitated the downward spread of corrosion in some cases, notably that of zinc in a chloride solution, where the two primary products (zinc chloride and potassium hydroxide) can co-exist for a sensible time before producing a coherent precipitate; but in most cases (*e.g.*, zinc in a sulphate solution) gravity appeared to play only a minor part, since even in specimens placed at an angle of only 20° to the horizontal, the spread of corrosion in the direction of low oxygen concentration was seen just as well on the lower side as on the upper side of the specimens. The uniform triangular groove left by the diamond point produced less marked corrosion than the irregular scratch made by a steel file. In the parts of the specimens near the water line, where the oxygen concentration was high, corrosion along the scratch lines frequently slowed down, or even ceased altogether, evidently because here the dissolved oxygen repaired the damage done to the skin.

All the observations made pointed to the fact that two mutually antagonistic changes were proceeding: (1) *direct combination* with oxygen, giving a protective oxide film; and (2) *anodic attack* of the metal, yielding a *soluble* chloride or sulphate (which, however, soon produces a sparingly soluble hydroxide by interaction with the alkali formed simultaneously at the surrounding cathodic area).

Where oxygen is in excess, the first change, and where it is deficient, the second change, will usually prevail. The mere fact that anodic attack has commenced does not necessarily preclude subsequent repair by oxygen, if supplied in excess; but if once sufficient loose corrosion product has been formed to prevent oxygen from diffusing to the metallic surface, the attack is not likely to be stopped at the points concerned.

In rolled unscratched specimens, local corrosion often set in at scattered "weak points"; some of these may have been caused by unintentional bending in the laboratory, but in many cases, at least, they represented defects originating in the rolling mill, or even in the foundry. Even where intentional scratches had been made, corrosion sometimes occurred at the natural defects in preference to the artificial. The pure zinc, as received, had many breaks in the smooth surface, in some cases revealing under the microscope marked elongated cavities. Unscratched specimens partly immersed in $M/10$-potassium chloride developed within about 30 minutes rings or loops of membranous zinc hydroxide, and in practically every case the microscope revealed a defect of the kind mentioned at the centre of the ring or loop. No doubt at such places the original oxide film will tend to be weak, and the inaccessibility of the interior of the cavities to diffusing oxygen will appreciably reduce the chance of effective repair, so that corrosion continues apace at these places. This represents, therefore, a case where the "cavity theory" appears to be substantially correct.

Besides starting at scratches and depressions, corrosion frequently started from "weak points" on and very near the cut edges; these appeared to result from the stresses produced by the slight bending which necessarily accompanies cutting; corrosion also occurred wherever there were kinks or crumples of any sort.

Numerous experiments were carried out to study the effect of bending on the corrosion of electrolytic iron, steel, and zinc. Narrow strips of finely ground metal were exposed to dry air or $M/10$-potassium chromate solution, and then bent in the centre around a glass tube; they were afterwards placed in porcelain dishes containing $M/10$-potassium sulphate or chloride; in most experiments on steel or iron potassium ferricyanide (2 g. per litre)

was also added as an indicator. Special corrosion was observed to set in at points situated on the bend; generally the convex side suffered more readily than the concave. Sometimes corrosion also set in at the ends where the specimen had been clinched with small pliers during the bending processes, but this was connected with the slight bending which the clinching involved; mere uniform pressure appeared to have very little effect. If the specimens were kept in air or potassium chromate solution for some hours between bending and immersion in the corrosive salt solution, the effect at the bend became less sharply defined, although corrosion still occurred at other places, notably over the "unaerated portion" where the bottom edge of the specimens rested upon the dish.

The results obtained with bent specimens are of interest in connexion with the author's observations on steel strips covered with thicker (visible) films of copper, nickel, and zinc (*Engineering,* 1928, **126**, 407). Here bending produced visible cracks, usually on the convex, sometimes on the concave, side; and corrosion commonly set in along these cracks. Mere pressure upon the film, however, even if intense, produced scarcely any damage to the film, and rarely led to corrosion. The close analogy with the new results suggests strongly that the corrosion produced by the bending of ordinary (unplated) iron, steel, or zinc is due to the cracking of an *invisible* skin of oxide or other compound. The residual stresses left in the metal itself, however, play an important part, because they tend to keep cracking or distending the films which are produced (after immersion) by the action of dissolved oxygen. Several examples of local corrosion set up by residual stresses have been seen during the present work, and the idea of film cracking may perhaps help to interpret the observations of others. Hatfield and Thirkell (*J. Inst. Metals*, 1919, **22**, 67) and Moore, Beckinsale, and Mallinson (*ibid.*, 1920, **23**, 225; 1921, **25**, 35; 1922, **27**, 149) have shown the effect of residual (internal) stresses on the corrosion of brass. Rawdon (*Ind. Eng. Chem.*, 1927, **19**, 613) has pointed out that the corrosion of several metals is facilitated by externally applied tensile stresses, and McAdam (*Proc. Amer. Soc. Test. Ma*[t.], 1926, **26**, ii, 224; 1927, **27**, ii, 102; 1928, advance proof) ha[s] studied the even more marked effect of alternating stresses on corr[o]sion (see also Speller, McCorkle, and Mumma, *ibid.*, 1928, advan[ce] proof). Finally, Bengough, Stuart, and Lee (*Proc. Roy. Soc.*, 192[7], *A*, **116**, 425) have found that different types of abrasion produ[ce] distinctly different values for the initial rate of the corrosion [of] zinc.

Apart from the intense *local* corrosion occurring at weak point[s] there occurs *general* corrosion on the lower parts of specime[ns]

which are inaccessible to repairing oxygen. This regional attack commences at the bottom of the specimen and gradually advances upwards, the upper boundary remaining usually straight and horizontal. The phenomenon may possibly be due to the film substance being itself permeable to anions; but microscopic examination of specimens taken out at different stages of the process suggests that it is really due to the occurrence of a large number of minor weak points placed so close together as to constitute almost uniform leakage. This leakage occurs only at places inaccessible to dissolved oxygen; where oxygen can penetrate, the minor weak points are kept in repair.

Experiments on Electrolytic Iron in Copper Salt Solutions.—It was shown in earlier work that iron exposed to dry air after grinding no longer reacts with copper nitrate solution, although it may still deposit copper from chloride or sulphate solution. No douht the fact that copper nitrate is itself potentially an oxidising agent may account for this. Provided that stresses are not present which keep cracking the film too quickly, the nitrate may perhaps itself help to repair the film; if cracking is too persistent, copper will he deposited. The effects of different types of local abrasion on the deposition of copper have now been studied. Uniform grooves made on air-passive iron hy a diamond cutter, a steel knife-point, or a smooth agate style were almost ineffective in producing deposition of copper, hut where the iron surface had been ahraded with jagged glass or with the edge of a carborundum wheel, rapid deposition of copper occurred. All types of ahrasion will leave internal stresses in the metal, but the stresses left by the diamond, steel point, or agate style will not be likely to produce cracking in the skin; on the other hand, the forms of abrasion which tear the surface will leave tangential stresses likely to keep the film continually in a cracked or distended condition. Moreover, the amond, steel, or agate leaves a smooth surface, whereas the sharp ass or carborundum leaves a jagged surface, usually with microropic undercut cavities, possibly containing fragments of the rasive.

Electrolytic iron (E 28) exposed to dry air for 24 hours after fine rasion, although hardly affected by $M/20$-copper nitrate (except a small extent at the cut edges), became covered uniformly with pper when placed in $M/20$-cupric chloride or sulphate; the loride gave a much less adherent deposit than the sulphate, and e copper colour (rather unexpectedly) appeared more slowly; the pidity with which the copper colour appears in the sulphate bath ay be the result of the good adhesion, since clearly the first traces copper, if in good electrical contact with the iron, will serve as a

cathode upon which further copper can be deposited. When iron which had been scratched locally was dipped for about a second in $M/20$-copper sulphate, washed quickly, and examined under the microscope, copper deposition was seen to have already commenced in the scratches, and sometimes the iron adjacent to the scratches was also plated with copper; the rest, however, was still bare. Scratching with jagged glass or carborundum promoted copper deposition most readily, but the diamond scratches also served as places where copper deposition would commence preferentially; abrasion with the agate style, which leaves a smooth gently rounded indent, seemed to have no effect in promoting deposition of copper.

In more concentrated ($M/2$) copper sulphate, the iron behaved *differently. For a few seconds, no change occurred visible to the unaided eye*, although specimens immersed for one second only, then quickly washed, dried, and examined under the microscope showed the production of traces of metallic copper along the cut edges. Specimens immersed for longer periods underwent a rapid alteration quite suddenly (often after about 10 seconds). Deposition of copper on the face commenced at certain points, usually along the edges, but sometimes (in half-immersed specimens) on the water line, or (in drop experiments) at the margins of drops. Sometimes deposition of copper commenced at other weak spots where the metal had been held with pliers or had otherwise suffered pressure or bending. Once commenced, the deposition of copper spread out with great rapidity until the whole surface was plated with copper. In some specimens, however, the extension of the copper deposit proceeded jerkily, being suddenly held up along certain irregular lines, along which, presumably, the protective film was specially adherent.

The different behaviour of dilute and concentrated copper sulphate solutions is easily understood. Deposition of copper at the cut edges involves anodic action upon the iron elsewhere. Anodic treatment of iron in a sulphate solution gives rise, as is well known, to soluble iron sulphate at low current density, but at high current densities other reactions become possible and the iron becomes oxidised and passive. Immersion of iron in dilute copper sulphate is equivalent to anodic treatment at low current density, and immersion in concentrated copper sulphate is equivalent to treatment at high current density. In this case the commencement of the attack at the cut edges and the extension of the areas through undermining of the skin are easily understood.

Possibly the behaviour of the iron towards copper nitrate is to be explained in a similar manner. Where large breaks occur in the oxide skin, replacement of iron by copper proceeds readily; the

necessary current density at the anodic portions being low. If the cracks are very small, the anodic current density involved in the deposition of copper is high, and the iron becomes oxidised, healing the cracks, so that the action does not develop. Of course, a smaller current density is needed to produce passivity in a nitrate than in a sulphate solution, and thus specimens of iron which fail to deposit copper from a nitrate solution may still react with a sulphate solution.

Experiments on Copper in Silver Nitrate Solution.—Finely ground copper, bent immediately after grinding and placed at once in $M/25$-silver nitrate, showed general blackening in a few seconds; there was no special phenomenon at the bend. Finely ground copper, kept for 9 days in a desiccator, then bent and placed in the same solution, showed marked deposition of silver all round the bend, and practically none elsewhere, except at small isolated points; whereas if it was bent and then exposed to air for 9 days it showed no special deposition at the bend, the exposure having apparently "healed" the damage to the film.

These experiments are important, for they appear to exclude a possible alternative theory. It might be argued that, since a distorted lattice is less stable than an undistorted one, strained metal should be anodic towards unstrained, quite apart from any question of film cracking. This is probably true, but it does not seem to be the cause of the phenomena actually noted at the bends, which appear only when opportunity has been given for the cracking of a protective skin.

Origin of Corrosion Currents.—If the new results are considered in conjunction with those obtained in previous work on the corrosion produced by dissolved oxygen, it appears fairly certain that the sites of local attack are weak points in a protective film of oxide. This is true of three important types of corrosion: (1) The corrosion produced by bending or stressing is due to the fact that the cracking of the film at the bends or stressed portion renders this part anodic to the rest. (2) Corrosion in pits and parts of the surface screened from dissolved oxygen by foreign matter is due to the fact that here the film is kept in less good repair than elsewhere, and consequently the "unaerated" portions are anodic to the rest. (3) Many instances of water-line attack are probably due to the fact that the protective skin adheres to the water–air instead of to the metal–water interface, thus exposing the metal. In general, the junction of different phases represents a point of weakness on a protective film. It is possible that the acceleration of corrosion by heterophase impu [illegible] ency of film failure to extend alo [illegible] remarkable

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fact that frequently non-conducting inclusions appear to be as potent in determining the sites of corrosion as conducting substances.

It must be recognised that there are many types of corrosion not determined by the distribution of films: these occur mainly in acid solution, where an oxide film would be dissolved. Thus, in the corrosion of impure zinc by acids, the corrosion currents flow between zinc and its impurities. Again, in the corrosion of copper, lead, and cadmium in acid solutions, electric currents may be set up by the unequal stirring of the liquid; the parts over which water flows most rapidly become impoverished in metallic ions, and are thus kept anodic towards the rest, suffering intense local corrosion. It is noteworthy that the chief metal which shows this "stirring current" really well, even in *neutral* solution also, is copper, a metal of which the oxide film has only a very weakly protective character. With zinc and iron in neutral solution, the points over which the water flows most rapidly usually become cathodic to the rest, owing to the increased supply of oxygen to these points.

It is fairly certain that in the types of corrosion mentioned above, the attack is connected with electric currents flowing between anodic and cathodic areas; in general, the insoluble corrosion product is a secondary product formed by interaction between the materials formed on the anodic and the cathodic areas. The currents set up by "differential aeration" have already been demonstrated and measured (*J. Inst. Metals*, 1923, **30**, 239); it is equally easy to demonstrate the current set up by bending one of a pair of similar electrodes; the bent electrode functions as anode, but by bending the other, the current can be reduced to zero, or even reversed.

Donker and Dengg (*Korrosion und Metallschutz*, 1927, **3**, 217) consider that the maximum *E.M.F.* available for the corrosion of iron is that of the cell iron|liquid|oxygen. This *E.M.F.* will theoretically fall between 1·0 and 1·2 volts according to the extent to which alkali is allowed to accumulate at the surface. In the author's opinion, these theoretical values are only likely to be realised if the "aerated" (cathodic) area has a film which is perfectly free from weak points. This is best seen if we consider the case of iron coated with a visible film of copper, instead of an invisible film of oxide. Several potentiometric tests of steel which had been coated with a porous layer of copper by the Schoop process showed that the *E.M.F.* of the cell steel|liquid|copper covered steel is definitely less than that of the cell steel|liquid|solid copper, and the *E.M.F.* of the former cell becomes smaller and smaller as the copper deposit is made thinner and more porous, a

is to be expected. It is not surprising, therefore, that the difference between the potentials of the anodic and the cathodic parts of ordinary (unplated) steel specimens corroded in *N*/10-sodium chloride solution under conditions of differential aeration has been found by McAulay and Bowden (J., 1925, **127**, 2605) to be only about 0·2 volt—far below the theoretical value. The question arises, however, whether a higher *E.M.F.* might not be obtained under specially favourable conditions.

Some attempts were made to measure the *E.M.F.* between aerated and unaerated steel under conditions such as to ensure a bountiful supply of repairing oxygen to all parts of the "aerated" area. The unaerated electrode consisted of a strip of finely ground steel fixed at the bottom of a glass vessel containing *M*/10-potassium chloride or sulphate, and for some days previous to the experiment kept joined by an external wire to a large piece of the same steel clamped above so as to pass through the water line. When the lower piece of steel was completely covered with rust, it was disconnected from the upper piece, and a narrow strip of steel was cautiously lowered until its lower edge just touched the surface of the liquid; regarding this as the aerated electrode, the *E.M.F.* between it and the lower electrode was measured on the potentiometer. The values obtained varied with different strips, and also with the time, but usually fell between 0·22 and 0·26 volt; although slightly higher than those previously obtained, these voltages are still far below the theoretical values.

In the arrangement just described, it was the edge of the upper electrode which was presented to the liquid; *i.e.*, a typical weak place was employed. In order to avoid this, strips of filter-paper were pulled into two, so as to leave ragged ends terminating in fibres. One of these was hung over the edge of the containing vessel, and when it had sucked up liquid, a fresh piece of finely ground steel was clamped so that the damp fibres of the ragged end of the filter-paper strip just touched the metal; the *E.M.F.* was then measured. In this way different points on the same piece of steel could be tested; as previously found by McAulay and Bowden, the readings varied considerably from spot to spot. Near the edges, the *E.M.F.* was always low, and sometimes low values were also obtained at points in the centre, which could often be correlated with definite defects in the surface; but for most points in the centre the values ranged between 0·42 to 0·49 volt both in chloride and in sulphate solution. With electrolytic iron the range appeared to be almost the same (usually 0·41—0·45 volt), with much lower values near the edge. Although the value varied considerably according to the position chosen for the test on the

aerated electrode, experiments in which three separate *unaerated electrodes* were fixed in the apparatus—capable of independent connexion to the potentiometer—indicated that it made but little difference which one of the three was used.

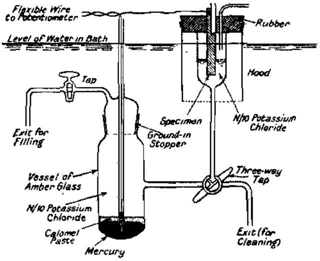
It is surprising to find that an *E.M.F.* of nearly 0·5 volt can be set up simply by differences in oxygen accessibility. It is still far below the theoretical iron–oxygen value, but it seems probable that the *E.M.F.* between perfectly film-free iron and iron covered with an "ideal" film free from weak places might attain the theoretical value if balanced on the potentiometer. Such an *E.M.F.*, however, would not operate during the corrosion process, since it was found that the *E.M.F.* always dropped rapidly when it produced a current (*i.e.*, when it produced corrosion). It was noticed that after the two electrodes had been short-circuited even for a few seconds, low values were obtained, which slowly rose again with the time.

Experiments were also carried out with zinc, two varieties of the metal being used in both chloride and sulphate solution; as found by McAulay and Bowden, the *E.M.F.*'s were lower than in the case of steel, but varied considerably with the positions on a single specimen; values between 0·10 and 0·17 volt were obtained. The low values are naturally connected with the fact that the protective skin on zinc is much less perfect than that on iron. It does not follow that the corrosion currents set up by zinc under differential aeration conditions will be lower than those of iron. On the contrary, the low values of the *E.M.F.* measured with zinc are probably to be ascribed to the flow of local currents on the aerated electrode which, of course, cannot be prevented by balancing the system on a potentiometer.

The Extension of the Breakdown.—In order to follow the early stages of corrosion before any change became visible, a potentiometer method was employed similar in principle to that used by May (*Engineering*, 1928, **126**, 309), and by McAulay and Bastow (preceding paper). The potential of iron covered with a discontinuous layer of another material lies between the potential of uncoated iron and that of the coating material, but the value depends on the degree of discontinuity. For instance, iron sprayed with a porous coat of copper shows a potential close to that of compact copper if the porosity is slight, but close to that of iron if the coating is highly discontinuous. Similarly, iron covered with a discontinuous oxide film should give a potential on the positive side of the potential of film-free iron; if the breakdown extends after immersion, the potential should move in a negative direction whereas if healing predominates, it should move in a positive direction.

The metals to be tested were rubbed with French emery No. 1, cut into strips 1 cm. wide, washed with alcohol, ether, and benzene, and mounted in the usual manner by means of rubber in wide glass hoods; they were then kept for 24 hours in a vessel containing calcium chloride and soda–lime (certain iron specimens were treated in $M/10$-potassium chromate). Each separate specimen had a hood of its own, which, during the period before the test, served to protect it from accidental bending; during the experiment itself the hood served to exclude atmospheric disturbances, and formed a water seal which allowed the specimen to be lowered, almost instantaneously, into the liquid without danger of stresses to the metal (see Fig. 2). The liquid employed was $N/10$-potassium chloride

FIG. 2.

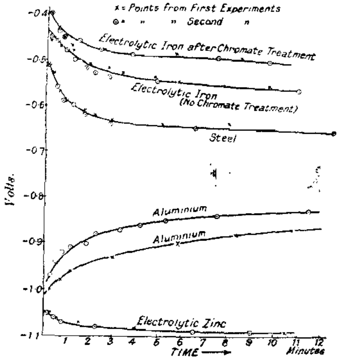


(previously shaken in a half-filled flask), and connexion was made through a three-way tap to a $N/10$-calomel electrode contained in a vessel of amber glass to prevent the disturbing influence of light on the potential; this vessel was completely full of liquid (no air space). Since the liquid was $N/10$-potassium chloride in both vessels, there was no appreciable error due to boundary potential. As the potential changed extremely rapidly, it was necessary to use a galvanometer detector, but the disturbance caused by passage of current was avoided by performing preliminary experiments which gave approximate readings for the potentials at different times, and these values enabled the potentiometer to be kept *nearly* in adjustment throughout the course of the actual experiments (with aluminium, this could not be done to the same extent, and the readings are probably less accurate). In these final experiments the values were obtained on a Weston voltmeter, checked against a Raaks instrument. Preliminary experiments showed that the

shape of the electrode was not important; an immersed area of 1·0 × 1·5 cm. was found to be suitable. Altogether 49 specimens were tested; a few of the results are shown in the curves of Fig. 3, times being measured from the instant of immersion; the temperature was 20°.

All these experiments were performed in duplicate. The iron, steel, and zinc specimens showed sufficient agreement between duplicates to be represented by a single curve, but the aluminium specimens showed much greater individuality. The curves indicate clearly that the breakdown extends less quickly on iron previously

FIG. 3.



treated with potassium chromate than on iron merely exposed to dry air for the same period—a conclusion previously reached by McAulay and Bastow (preceding paper)—and also that the breakdown on steel occurs more quickly than that on pure iron. The final values of all three materials, reached after 22 hours, are, however, approximately the same for steel, iron, and chromate-treated iron. Zinc shows from the very first a value within 0·04 volt of the final value, indicating that the oxide film on this metal has only a very small protective value; however, a small but genuine drop was shown by all the zinc specimens tested.

Unlike iron, steel, or zinc, the aluminium specimens showed a marked rise in potential with time. This appears to indicate that on this metal the weak points tend to "heal," and the conclusion

s supported by the observations made later when the changes inally become visible; whereas the corroded areas on zinc, iron, ind steel appear as patches which rapidly extend until they cover nore than half the immersed surface, the corroding points on iluminium during the same period remain of microscopic dimen- ions. Although individual aluminium specimens showed different urves, all the specimens tested displayed this rise. Specimens of iluminium ground only 5 minutes before the experiment, however. howed a temporary fall in potential after immersion, followed by a nuch greater rise; no doubt, at first the stresses left by the recent ibrasion permitted the breakdown to extend temporarily, but as soon as the stresses were relieved thereby, the healing influence began to predominate once more.

Another series of experiments was carried out in sulphate solu- ions; here the general form of the curves was the same, but the values have no absolute significance, owing to the error due to liquid boundary potentials.

Since this work was finished, French and Kahlenberg (*J. Amer. Electrochem. Soc.*, 1928, advance proof) have published a study of the effect of oxygen, hydrogen, and other gases on the potential of various metals. They consider that the alteration of the potential s "due both to absorbed gas and a condensed film of gas." The uthor agrees with many of the views put forward, but considers hat the effect of oxygen on such metals as iron is much more atisfactorily explained by taking into account the effects of the liscontinuous oxide film. In any case, the superior effect of potassium chromate over that of air, in elevating the potential, and the disturbing effect of surface weaknesses and residual stresses, can hardly be explained simply by considering absorbed and condensed gases.

Undermining and Flaking.—Closely allied to "passivity" is the phenomenon known as "flaking." Bengough, Jones, and Pirret (*J. Inst. Metals*, 1920, **23**, 80) found that when specimens of drawn brass were immersed in dilute ammonium nitrate solution the reagent penetrated below the surface, undermining the surface layers, which in the course of some weeks, could be peeled off; the thin films thus removed consisted of uncorroded brass and were about 0·01 mm. thick. A similar effect was afterwards obtained with rolled zinc by the author (*J. Soc. Chem. Ind.*, 1926, **45**, 42T).

The tendency for corrosion in rolled or drawn material to proceed parallel to the surface is readily explicable. Any type of attack which preferentially follows the crystal boundaries (whether it be attributed to intercrystalline impurities, intercrystalline cavities, or "amorphous" metal) will advance most quickly in this direction,

since in worked materials the crystals are elongated parallel to the surface; the arrangement of non-attackable inclusions in planes parallel to the surface will also form barriers tending to deflect the attack in the direction in question—an important matter in the corrosion of wrought iron (*ibid.*, 1928, **47**, 62T). But it is still necessary to explain why the surface layers of the metal should not be corroded away, leaving only an oxide skin, as was actually found to be the case with passive pure iron (J., 1927, 1020). We appear at first sight to be dealing with cases where the "protective film" consists, not of an oxide, but of the metal itself; and it is specially puzzling to meet this in a metal such as zinc, where, according to Russell (*Nature*, 1925, **115**, 455), two different electronic configurations of the metallic atom are not to be expected.

A series of microscopic observations has shown, however, that *there is no sharp distinction between undermining of the surface in zinc and the stripping of the protective skin from passive iron.* If pure iron is coarsely ground and coated with an oxide film either by heat-tinting in air or by treatment with potassium chromate solution, and the film is then undermined and removed by means of iodine, it is found to consist almost completely of oxide, with occasional specks of opaque metallic iron. If, however, the metal has been ground with a very fine abrasive before being rendered passive, treatment with iodine isolates flakes which show a framework of metal supporting "windows" of very thin oxide film. With aluminium, both the iodine method and the anodic method of isolating the surface film give flakes which are partly metallic, although in places the transparent oxide film, bearing the original marks of abrasion, can be seen free from any metallic support. It was found that the flaking which occurred when rolled zinc was immersed in *M*/10-potassium chloride or sulphate for some weeks was merely an extreme example of the same effect. To the naked eye the flakes appeared metallic and opaque; on treatment with dilute acid they dissolved quickly with effervescence; but a microscopic examination showed that some of the fragments were quite transparent in places, and in some cases it was possible with a wire point under the microscope to break the flakes into parallel layers. After considerable microscopic study, the opinion was formed that the flakes consisted of alternate layers of metallic zinc and zinc oxide.

The key to the phenomenon is provided by the work of Stead (*J. Iron and Steel Inst.*, 1921, **103**, 271), who found that iron heated to a high temperature in air suffered intergranular oxidation, the oxygen penetrating between the crystals, and separating them by a sheath of oxide. No doubt at lower temperatures the same

phenomenon can occur, but the oxide sheath will be thinner (invisible in sections) and will not penetrate so far. In rolled metal we may expect the debris of flattened grains composing the surface layers to have a certain amount of oxide between them; possibly the rolling may actually help to introduce oxide below the surface. Doubtless the subcutaneous oxide sheaths will not be continuous, but they will make the attack of the surface portion of the metal, either from above or below, a slow matter; the portion of the metal further from the surface will be corroded more quickly. Hence arises the undermining and loosening of flakes consisting partly of metal and partly of oxide, in proportions depending on the chemical and mechanical properties of the metal and on its previous treatment.

It remains, however, to consider why the film removed from iron which has been coarsely abraded before being rendered passive consists almost wholly of oxide. It would seem that here the violent abrasion produces a series of cracks through which the oxidising agent can pass, thus converting into oxide the portions of metal which would otherwise be isolated between oxide sheaths, and leaving only specks of metallic iron here and there. Such specks are actually seen in the microscopic examination of the separated film, and are arranged in an ordered manner connected with the abrasion directions. In metal which has been only gently abraded, less cracking occurs and the main function of the oxidising agent which produces the passivity is simply to repair any damage to the oxide film already present on the exterior surface.

Müller (*Z. Elektrochem.*, 1928, **34**, 583), in commenting on the author's previous work (J., 1927, 1020), accepts the view that the inertness shown towards copper salts after exposure to air or potassium chromate is due to a protective film, but considers that the passivity obtained by anodic treatment in acid solution cannot be ascribed to such a cause. He finds that iron rendered passive by exposure to air quickly deposits copper from an acidified copper salt solution, and that the time needed to produce passivity by anodic treatment of air-exposed iron electrodes is practically the same as that needed in the case of freshly polished electrodes. Moreover, iron which has been rendered passive by anodic treatment resists rusting under conditions which cause rusting of active iron. He concludes, therefore, that films play no part in causing anodic passivity, and that active and passive iron represent different states of the metal.

The facts brought forward by Müller accord well with the author's own experience. The film produced by the direct action of dry air or iron never survives such drastic conditions as Müller has

employed. It breaks down, for instance, in the presence of chlorine ions (usually even sulphate ions), the attack setting in at any of the weak places which are not sufficiently supplied with the dissolved oxygen necessary for constant repair. But if the iron itself is already supercharged with oxygen by previous anodic treatment, there is no reason for this breakdown to occur, whatever be the distribution of oxygen in the solution; as soon as the charge of oxygen is removed by suitable cathodic action (*e.g.*, by contact with zinc), the iron becomes capable of rusting, and this Müller has found.

The fact that the mild passivity produced by air-exposure is dispelled by acid-treatment does not mean that the anodic actior may not in due course produce a new film. As Müller has so neatl demonstrated, passivity does not set in during anodic treatment i sulphuric acid until the liquid layer next to the metal has becom saturated with the metallic sulphate (or some other substance which is seen separating out; when it is so saturated, the liqui has presumably lost its power to dissolve any oxide or other fil which may be present on the metal. On the whole, Müller's ne experimental results appear to support the view of anodic passivit developed by Hedges (J., 1928, 976).

Summary.

Breakdown of the protective film on iron, steel, zinc, or aluminiu tends to occur where the surface has been bent or cut, or whe rolling or casting defects occur at the surface; at these points loc corrosion sets in, and usually spreads out, although where dissolv oxygen is in excess the weak point often heals up again and t corrosion does not develop. Pre-existing cavities may determi the sites of corrosion, as in zinc, their interiors being inaccessil to repairing oxygen; but this cannot be a common cause of localis attack, which can be obtained under anaerobic conditions if external *E.M.F.* be applied. Internal stresses are important determining corrosion if they are of such a character as to keep t film in a state of weakness. "Differential aeration currents" due to the differences of potential existing between the places wh the film is kept in repair by the presence of oxygen and th where it is not kept in repair; *E.M.F.*'s approaching 0·5 volt to this cause have been measured, but the *E.M.F.* falls off whe rrent actually flows. The extension of breakdown, or the re he film, can be followed by potential changes.

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XVII.—*The Mechanism of Corrosion.*

By Ulick R. Evans.

The present paper describes a study of the corrosion of partly immersed specimens of zinc, iron, steel, aluminium, and copper in potassium chloride and sulphate solutions, with special reference to the thin films which give rise to interference colours in certain parts of the specimens. Hitherto these colours have been regarded as the result of direct oxidation of metal where the original film has been rendered pervious by cathodic or incipient anodic action; but the fact that the second-order colours are far brighter than the second-order " temper colours " produced by heating in air, suggests that they are really due to precipitated hydroxide, not anhydrous oxide. The films commonly found on the glass surface of vessels in which iron specimens have been corroded—although showing the ordinary rusty yellow colour of ferric hydroxide by scattered light—show similar bright high-order colours by regularly reflected light; these films on glass must be produced by precipitation or hydrolysis, and it appears probable that the colours formed on the metal itself are due to soluble iron salts diffusing through the original protective skin into a liquid containing excess of alkali, which precipitates the iron as a uniform film of hydroxide as it emerges. This view is supported by observations on copper and aluminium, where similar colours pass continuously into thicker, less uniform, deposits which are undoubtedly formed by interaction of soluble copper or aluminium salts with the cathodically formed alkali. The idea that the tints on iron are due to hydroxide was first suggested to the author by Professor Fearnsides.

The colour sequence is always essentially the same as that observed in the case of silver iodide films on silver. The colours belonging to different " orders " may be distinguished by Roman numerals, thus: yellowish-brown I, reddish-mauve I, deep blue I, greenish-blue I, steely silver, (hiatus), yellow II, red II, blue II, green II, yellow III, red III, green III, red IV, green IV, red V. On zinc and aluminium, partly owing to the transparent character of the film substance, the early colours are weak, for reasons given elsewhere (*Chem. Ind.*, 1926, **45**, 213). In general, the colours cannot be seen when the specimens are in the liquid, and a new procedure was therefore adopted. Numerous identical specimens, which had been simultaneously submitted to corrosion, were successively withdrawn, washed, dried, and examined microscopically. The series thus produced provided a narrative of the various changes, which revealed many facts previously overlooked.

Eight materials have been examined—electrolytic zinc, commercial zinc, electrolytic iron (two varieties), steel (two varieties), aluminium, and copper—the analyses being given in the preceding paper. These were studied under numerous different surface conditions; the description "rolled surface" denotes the original rolled metal, washed with benzene and alcohol but not abraded, and the terms "coarsely ground," "finely ground," and "very finely ground" imply abrasion with emery paper No. 2 (Oakey), No. 1 (French), and No. 000 (French), respectively. Two liquids were employed, *viz.*, $M/10$-potassium chloride and $M/10$-potassium sulphate.

Qualitative Results.

In the description of the qualitative work, the term "partly immersed strips" is used to denote strips about 6 cms. long and 2 cms. wide, placed in glass vessels at an angle of 70° and immersed to a depth of 4 cms., the four corners resting against the glass. Only a bare summary of the results obtained from several hundreds of specimens can be given.

Zinc.—Finely ground, very finely ground, or rolled specimens in $M/10$-potassium sulphate soon develop tiny white spots at "weak points" distributed in the manner indicated in a former paper, and from these spots descend narrow ribbons of adherent white matter; the whiteness (seen by scattered light) is most intense at the point of origin, indicating that the deposit is here thickest (the sequence of interference tints, when visible, confirms this).

During the first 40 minutes after immersion, all this white matter is *adherent*; no cloudiness is produced in the liquid. The cause is clear. Over an area of weakness, the film is virtually porous, and at each pore the exposed zinc is anodic towards the oxidised neighbouring metal; the anodic and cathodic products, zinc sulphate and potassium hydroxide, thus appear side by side and interact so close to the metallic surface that the zinc hydroxide adheres to it. The deposit of zinc hydroxide will clearly not at first be of uniform thickness, and at low thicknesses, interference tints are not conspicuous, but as the deposit develops, the thickness naturally becomes more equal and the later tints can usually be seen, provided that the surface conditions be suitable; on very finely ground zinc, the earliest colours from yellowish-brown [illegible] upwards have been detected. The deposit of precipitated hydroxide shields the metal below from the repairing action of oxygen, thus assisting the corrosive action to spread, particularly in the direction of low oxygen concentration. Hence the whitened area extends downwards. But, clearly, when the adherent zinc hydroxide covers [illegible]siderable area, it will prevent any cathodic reaction on the

area, since such a reaction requires oxygen; it is evident that the alkali must now come from the uncovered zinc outside the whitened area. Consequently there is produced along the borders of the white streak a membranous wall of zinc hydroxide, growing *outwards at right angles to the metallic surface* and enclosing the white streak like the finger of a glove; simultaneously, the liquid begins to be cloudy, and finally a precipitate, formed by interaction of zinc sulphate and potassium hydroxide which have met far away from the metallic surface, begins to settle to the bottom of the containing vessel.

Outside the membranous wall of zinc hydroxide, alkali is now in excess. Any leakage of zinc sulphate through imperfections of the skin will here produce an adherent film accurately parallel to the metallic surface, which will therefore be less white by scattered light, but will show better interference tints by reflected light than the adherent deposit produced within the membranous wall. Thus we get a series of coloured bands running parallel to the membranous wall and just outside it, the colours indicating that the film is thickest next to the wall, and especially at the parts nearest to the original area of weakness.

We must, therefore, distinguish four different types of zinc hydroxide, all produced by precipitation where zinc sulphate and potassium hydroxide meet:

Type A, produced when zinc sulphate and potassium hydroxide are formed at numerous points side by side on the metallic surface; this is closely adherent, not removed hy rubbing, very white (by scattered light), but showing only poor interference tints or none at all.

Type B, produced when zinc sulphate and potassium hydroxide are formed over two separate areas; it constitutes a membranous wall at right angles to the metallic surface, following the junction of these areas; it adheres weakly to the metal, being easily rubbed off, and leaving simply a whitish line to show where the wall has been.

Type C, produced when zinc sulphate and potassium hydroxide meet far from the metallic surface; it is a flocculent precipitate, and sinks to the bottom of the vessel, or rests as a loose non-adherent blanket on the lower part of the specimen.

Type D, produced when zinc sulphate oozes through a defective oxide skin into liquid containing potassium hydroxide in excess; it constitutes a very regular film, with good interference tints, and only showing whiteness when it reaches considerable thickness.

The corrosion which commences simultaneously at numerous weak spots (especially on or near the cut edges) doubtless uses up

much dissolved oxygen at the cathodic areas; the repairing power is thus impaired, and so streaks of zinc hydroxide commence to descend from fresh points higher up; these streaks usually broaden as they descend. Also at the bottom of the specimen, where oxygen becomes completely exhausted, a continuous whitened region appears bounded by a horizontal upper boundary, which advances steadily upwards with the time. Within a day from the start, nearly the whole surface has become covered with zinc hydroxide, with the exception of a narrow area near the water line; this is separated from the corroded area below by the sinuous "mantle" formed by the union of the membranous fingers mentioned above: frequently the tops (domes) of the mantle touch the water level. In general, the greater part of the area below the mantle suffers corrosion in the later stages, being covered with a blanket of precipitated zinc hydroxide which shuts off the supply of repairing oxygen. Samples of the pure zinc with a very finely ground surface show in the later stages microscopic grey points arranged along the abrasion lines; these are points where the zinc has been sc much corroded that the original whitened surface has disappeared and they become more and more frequent as the original areas o weakness are approached, becoming there practically continuous.

The portion above the mantle constitutes the cathodic zone ir the final stages, and suffers comparatively little corrosion. A serie of little white points appears along the water line itself—a plac where a protective film usually breaks down—but, doubtless owin to the good supply of repairing oxygen and of alkali, the amoun of corrosion here is trivial. A small amount of adherent hydroxid is produced, the white points uniting in the later stages to form continuous line along the water level, whilst colours spread down wards from the water line as roughly horizontal bands, the sequenc indicating that the film is thickest near the top, where blue I o even red II is commonly reached. A thin scum of membranou zinc hydroxide is often seen floating on the water surface.

In the later stages, the alkali produced plentifully over the mai cathodic zone causes the liquid to creep up the surface above th water level, and at the top boundary of the area wetted by creepag further small quantities of zinc hydroxide are formed; betwee this and the water line the surface displays second- or third-ord interference tints.

Whilst on rolled zinc and even on finely ground zinc, corrosic commences at well-defined points, on coarsely ground zinc the pr duction of zinc hydroxide is less severely localised, evidently owir to the larger number of weak points. Likewise, in $M/10$-potassiu chloride solution the corrosion product has a rather more diffu

aspect than in sulphate solution; thus, finely ground specimens of the commercial zinc in chloride solution somewhat resemble coarsely ground zinc in sulphate solution. The corrosion extends less quickly than in a sulphate solution under the same conditions of surface, but seems to commence at a greater number of points. On finely-ground pure zinc, the final line of the mantle is invariably more sinuous in chloride than in sulphate liquids; the appearance suggests that many weak points which can become effective centres of corrosion in chloride solutions do not function as centres of attack if the larger (SO_4'') anions alone are present. Pure zinc gives more sharply defined white points than commercial zinc—possibly another sign that impurities aid the extension of the areas affected by the breakdown.

The difference observed between the effect of chloride and sulphate solution is in part due to the different flocculating powers of the two species of anions. A series of experiments was conducted in which $M/10$-potassium sulphate containing small quantities of alkali ($M/200$) was added in varying amounts to $M/10$-potassium sulphate containing small quantities of zinc sulphate ($M/200$); parallel experiments were carried out with $M/10$-potassium chloride solution. It was found that, for corresponding proportions, precipitation of zinc hydroxide occurred far more quickly in the sulphate than in the chloride liquid; in order to obtain the same rate of precipitation a smaller amount of alkali was needed in sulphate than in chloride—this is no doubt due to the fact that SO_4'' and OH' ions have a far greater flocculating power than Cl' ions. Evidently in a sulphate solution we may expect to find zinc hydroxide produced close to the seat of corrosion, whilst in chloride solution the soluble zinc chloride will have to wander further into the alkaline region before yielding a precipitate. Thus even in the early stages, the corrosion product formed in the chloride solution is largely non-adherent; at a weak point, instead of a dense adherent white spot, we get a somewhat gelatinous " blob " or (in the case of the pure zinc) a loop-shaped membranous wall of zinc hydroxide extending out at right angles to the metallic surface, and enclosing the point of attack on three sides.

Aluminium.—The commencement of corrosion on aluminium is not unlike that on zinc, but since the oxide film is of a protective, self-healing character, the corrosion remains localised at points for a long time instead of becoming general. The attack develops more quickly in chloride than in sulphate solutions, although in both solutions it is very slow. In rolled specimens the corrosion product appears as an adherent white deposit at points along blemish-marks, and also at the edges and along the water line; on

abraded specimens there are numerous microscopic white points arranged on the groove-lines. The water-line attack is relatively more important on aluminium than on zinc; the fact that the corrosion over the lower part of the specimen is very slow must mean that the oxygen consumption is low; consequently there is not likely to be an appreciably higher oxygen concentration at the water line than elsewhere, and the special factor militating against water-line attack on zinc is therefore inoperative in the case of aluminium.

The corrosion product (aluminium hydroxide) remains adherent for much longer than in the case of zinc. In sulphate solution, practically the whole is still adherent after 4 days, the liquid being only very slightly cloudy; in chloride solution there is more cloudiness, and near the edges of coarsely abraded specimens, there is some fluffy aluminium hydroxide; after 15 days, there is much settled flocculent precipitate in chloride solutions, and some in sulphate solutions.

On rolled specimens, the adherent corrosion product formed in the early stages constitutes such a uniform layer as to produce interference tints; these commence from the weak points as circles, usually somewhat elongated downwards, the most advanced tints being in the centre; above the first-order tints, the rings show distinct white cloudiness, which is very intense in the centre; when held at the proper angle, the scattered light from the cloudy inner rings shows colours complementary to those seen by regularly reflected light (a common optical phenomenon). One specimen taken out after 4 days in the sulphate solution displayed first-order yellow over the main part of its surface, although the yellow was so faint that it might have escaped notice but for the fact that it passed gradually into the higher colours. The second- and third-order colours visible under the microscope around the points of breakdown are very clear and beautiful; one specimen taken out after 7 days showed the entire sequence from yellowish-brown I to red V around one centre of breakdown. Near the water level the colour rings are very numerous and somewhat elongated in a horizontal direction, sometimes uniting to form bands of colour roughly parallel to the water line.

It is interesting to correlate the results with those observed on zinc. On aluminium, hydroxide of flocculent type C is only produced at a late stage, whilst the membranous type B is usually absent; this allows the two adherent types A and D to pass gradually into one another, instead of being sharply divided at the mantle line as in zinc.

Iron.—The attack on iron commences in a similar manner t

that on zinc. Green points appear near the edges, also on rolling defects, and sometimes on abrasion marks, and spread downwards and to some extent sideways, producing arch-shaped green areas; at first the green deposit is adherent, as on zinc, but after a time a membranous wall (brown on the outside, green within) appears round the edge of each green area, and about the same time cloudiness appears in the solution, a green or brown precipitate finally settling to the bottom. Later, above the membranous wall, bright interference tints appear. Thus four types of corrosion products are obtained, analogous to the types A, B, C, and D obtained with zinc, but the question is complicated by the fact that the product varies from ferroso-ferric hydroxide (green) to ferric oxide (brown) (compare Scholten, *Korrosion u. Metallschutz*, 1928, 4, 73).

The behaviour in chloride and sulphate solutions is much the same, but on steel H 28 there is a greater tendency for streaming to occur from central weak points in chloride solution, whilst in sulphate solution central streaming is seldom observed; the etched areas usually descend in graceful curves from points on the cut edges, whilst at the bottom regional corrosion commences with horizontal boundaries gradually moving upwards. The differences between chloride and sulphate solutions are no doubt due to the greater penetrating power of chlorine ions. On the whole, electrolytic iron behaves like steel, but specimen E 28 shows a greater tendency to the production of central points of streaming than steel H 28, which has a similar thickness; probably this is simply because the steel contains fewer rolling defects. On the other hand, *ceteris paribus*, there is a greater tendency for "healing" to occur when impurities are absent. Thus within an hour of introduction into either sulphate or chloride solution, one series of strips of thin electrolytic iron (E 26) showed streaming from certain surface defects; but corrosion from these points soon ceased to develop, and after 21 hours it was confined to a region at the bottom bounded by a straight horizontal line.

Specimens when taken out always show the corrosion near the water line to be very slight; indeed it is usually impossible to detect the place at which the water level has been. As explained in discussing aluminium, water-line attack only occurs where the corrosion is slow enough to leave the oxygen concentration almost uniform. This may occur, with iron, if corrosion is retarded by the presence of a film-repairer, such as potassium chromate, in the solution, or of chromium in the metal.

Specimens of sand-blasted steel behaved somewhat differently from abraded steel. The sand blasting evidently produces a systematic distribution of weak points, and each becomes marked

by a little tuft of rust. A true mantle is always formed, separating a highly corroded area below from a very slightly corroded area above. The number of tufts of rust per unit area above the mantle is roughly the same as that below, but whereas those below the mantle almost join to form a continuous blanket, those above are of microscopic dimensions. The case is interesting, since it displays superimposition of two effects—those of (1) the original mechanical treatment, and (2) the distribution of oxygen in the liquid.

Copper.—The oxide film on copper is less protective than that present on most other metals; when this is remembered, the observations made on the corrosion of copper in chloride and sulphate solutions fall into line with those on zinc, iron, and aluminium. The behaviour varies greatly with the abrasive treatment used, as was shown by parallel experiments with abrasives of six different degrees of coarseness.

Very finely ground samples of copper placed in potassium chloride solution soon develop sharply-defined brown points, situated mainly near the edges and bottom; those situated in the centre spread out in all directions, but most rapidly downwards, producing little oval areas; the dark matter on these areas is adherent, and specimens taken out at intervals reveal a series of rich but dark interference tints, the colours indicating that the film is thickest near the point of origin; corrosion from weak spots near the edge extends inwards as horizontal streaks following the principal grinding direction, and these also pass through colour changes in the usual sequence. The colours gradually spread until they cover the greater part of the submerged surface; there is no membranous corrosion product, and, as in aluminium, there is a gradual transition from deposits of type A into type D. On the more coarsely ground specimens, dark matter appears as larger irregular patches, with boundaries related to the grinding direction, but rather vaguely defined; this material is somewhat more loosely adherent and discontinuous; the dark patches are surrounded by a paler zone of brownish deposit which exhibits variations of tint probably produced by interference; presumably this corresponds to the type D deposit on zinc, whilst the dark material corresponds to the type A deposit. The pale brown zones spread rapidly over the whole surface, followed by the darker areas, which, in the more coarsely ground specimens in potassium chloride solution, often cover the whole immersed area after 21 hours, apart from a narrow band at the water line. Examination of specimens taken out from chloride solutions has shown that two constituents are present in the adherent deposit, one black and quickly dissolved by very dilute hydrochloric acid, the other red and less quickly dissolved. Presumably these

are respectively cupric and cuprous oxide. Probably the immediate products of corrosion are cuprous chloride and potassium hydroxide, and the former, being sparingly soluble, is acted on by the alkali *in situ*, yielding cuprous oxide, or where oxygen is present in excess, cupric oxide. A certain amount of white cuprous chloride can still be seen in the deposit.

After 3 days a new phenomenon sets in. The dark areas covered with the "Type A" deposit begin to develop a greenish substance upon the dark oxide layer, whilst the liquid becomes cloudy, and finally greenish-grey matter settles to the bottom of the vessel. The green matter appears to be mainly basic cupric chloride, and is probably produced by the action of dissolved oxygen on the cuprous chloride according to the reactions suggested by Bengough and May (*J. Inst. Metals*, 1924, **32**, 115). About the same time, breakdown of the protective film occurs along the water level, where a green line of corrosion product gradually develops, which easily rubs off, revealing bright copper sensibly corroded. The water-line corrosion is most serious on the coarsely ground specimens, but the formation of green matter on the lower part of the surface, and on the bottom of the vessel, is most rapid on finely abraded specimens.

In potassium sulphate solution, the early phenomena are somewhat similar, but the dark deposit extends less quickly over the surface, and in general shows less brilliant colours. In the later stages the deposit appears to contain a greater proportion of the black and less of the red constituent than the deposits formed in chloride solution. Probably the primary products are cuprous sulphate and potassium hydroxide, but the former no doubt begins to decompose before interacting with the alkali, thus accounting for the usually rather "dirty" character of the deposit, and the higher ratio of cupric to cuprous oxide; the deposit has a whitish appearance when held in certain lights, and this may conceivably be due to small amounts of surviving cuprous sulphate. In contrast with chloride solution, there is even after 30 days no appreciable cloudiness or settled deposit in the vessel, but slight water-line corrosion occurs on the coarsely abraded specimens.

Quantitative Results.

In the quantitative work, the strips were clamped at the dry part above the water line so that they stood vertically and in a central position in beakers 9 cms. high and 4 cms. in diameter; the metal did not touch the glass (or any solid) anywhere on the immersed area, and except in series B, the specimens were abraded 24 hours before the experiment with No. 1 (French) emery, and

were washed with alcohol, ether, and benzene before being weighed The glass beakers were themselves placed in a closed copper bo: sunk in a thermostat bath, and fed continuously with a stream o purified air (or oxygen in sub-series A1). To prevent the otherwis serious loss of heat by radiation from the copper lid, this was covere with asbestos (separated from the copper by a narrow air space) and the whole thermostat, which was electrically stirred, controlled and heated, was placed in a cupboard with asbestos lining. Th last of the 9 vessels comprising the purification train was also place in the cupboard (the temperature of which differed by only few degrees from the bath itself), and from this the air passed throug a metal coil placed in the bath before it entered the box; it emerge from the box through a water trap.

Every experiment was carried out in duplicate. Each point c the curves shown in Fig. 1 depends on a different pair of specimen and thus the curves are fairly representative of the whole materi and not of a single piece. (In the oxygen-absorption method, whe the complete curve is derived from a single specimen, the poin necessarily fall better on a single curve, but it does not follow th the same curve would be given by other specimens.) The agreeme between duplicates is often rather poor in the early stages, bet in the middle, and extremely poor in the final stages; in the mid stages the variation from the mean is similar to that obtained Bengough, Stuart, and Lee (*Proc. Roy. Soc.*, 1927, *A*, **116**, 42 who measured the oxygen absorption during the corrosion of ho zontal specimens, but in the later stages the reproducibility is ve much worse than that obtained by these authors, whose method greatly to be preferred for obtaining equations connecting corros and time. Specimens cut from certain portions of the steel sh were found to corrode perceptibly more quickly than those ta from other regions. For that reason, specimens to be compa within a single series were taken, as far as possible, from contigu portions. In this respect Series A and B are not strictly compara to Series C.

In spite of the valid objections to the partial-immersion meth there are several reasons why the corrosion of partly imme specimens is specially worthy of quantitative study. (1) Nearl the conditions which cause serious corrosion in practice are wa line conditions (the margin of drops may be included within term "water line"). (2) The method ensures a free suppl oxygen to the metal at the water line, and thus it is possibl avoid the unsatisfactory conditions (met with in much of the e work on completely immersed metallic specimens) where sev materials capable of corroding at different rates under condi

of excess of free oxygen, actually have been found to corrode with the same velocity, this velocity being imposed by the limited rate of supply of dissolved oxygen. (3) If the specimens are clamped above the water line, the disturbing influence of differential aeration around the point of support is avoided. (4) In vertical specimens, the *corrosion—although starting locally*—usually soon spreads and becomes fairly general; with horizontal specimens, the same spreading occurs, but more gradually. (5) The insoluble corrosion product in vertical specimens is largely precipitated in a non-adherent form, easily removed by wiping; there are no pits to retain the product; in the case of iron and steel, the error caused by the small amount of corrosion product not removable by wiping is probably less than the weighing error.

In the case of zinc, however, the error due to closely adherent matter is still appreciable, for specimens which had been corroded for 24 hours, if rubbed with very fine emery paper until the adherent white matter was removed, lost additional weight; undoubtedly this loss was partly due to the grinding away of metallic zinc, as well as of corrosion product, but the results suggested that the true corrosion loss was distinctly higher (by about 10%) than the loss of weight would suggest. In the 70-hour experiments, the creepage of the cathodically formed alkali above the water line caused the presence of a very large amount of closely adherent corrosion product, so that here the figures for the decrease in weight are valueless as a measure of corrosion. It is likely that the 48-hours results with zinc were slightly vitiated by the same cause. It may be added that experiments extending over several weeks again show a reduction in the error due to adherent product; only a limited amount of corrosion product can adhere, and this becomes continuously less important as the total corrosion increases; the agreement between duplicates also becomes better again, as shown in previous work.

When aluminium was investigated, the error due to adherent matter became so serious that in the early stages the change in weight entirely failed to represent the corrosion. Both in sulphate and chloride solution the alteration in weight was small: in all experiments up to 48 hours, it was less than 1 mg. The corrosion product formed on specimens exposed for short periods (4—14 hours) was such that it was nearly entirely removed on wiping, and consequently the specimens lost weight; but on longer exposure to the corrosive medium (48 hours), the product underwent a change (probably the well-known "ageing" of hydroxides) and became tightly adherent, so that the specimens even after wiping were found to have gained weight. Experiments (not carried out

in a thermostat) extending over several weeks indicated that on long immersion a large amount of loose precipitate of type C was formed, and consequently specimens lost weight again. It is evident that here no conclusions can be drawn from the alterations in weight. The qualitative inspection of specimens, however, makes it quite certain that the corrosion of aluminium is very slow compared to that of zinc and iron. In considering the change in aluminium hydroxide, it is interesting to recall that a change in the physical properties of iron rust occurs on storage (Aston, *Trans. Amer. Electrochem. Soc.*, 1916, **29**, 449), whilst the oxide film produced on aluminium by exposure to air at high temperature also undergoes a spontaneous change very suddenly, becoming impervious to oxygen (Pilling and Bedworth, *J. Inst. Metals*, 1923, **29** 573).

The results of the quantitative experiments are given in the tables below; the data of Series C are plotted as curves in Fig. 1 the 70-hour experiments are omitted for reason given above.

Series A.

Effects of shape of electrode in (1) oxygen and (2) air.

(All electrodes were cut from steel H 28 and finely abraded. Experiments were conducted for 22 hours at 25·0°.)

Breadth of specimen, cms.	Depth of immersed portion, cms.	Solution.	Loss of weight, mg. (1).	Loss of weight, mg. (2).
1·2	3·0	*M*/10-KCl.	9·3, 9·7 } 9·5	3·8, 4·0 } 3·9
2·4	2·0	,,	14·7, 15·5 } 15·1	5·6, 5·8 } 5·7
2·4	3·0	,,	16·5, 16·6 } 16·5	6·4, 7·4 } 6·9
2·4	4·0	,,	16·6, 17·4 } 17·0	7·2, 7·2 } 7·2
2·4	3·0	*M*/20-KCl.	15·3, 16·8 } 16·0	6·6, 5·7 } 6·1

Series B.

Effect of abrasive treatment.

(All specimens were cut from electrolytic iron, E 28, ground with differ grades of French emery, and corroded for 8 hours at 25·5°. Immer area = 2·5 × 2·5 cms. in each case. Liquid, $M/10\text{-}K_2SO_4$.)

Grade.	Loss of weight, mg.	Grade.	Loss of weight, mg.	Grade.	Loss of weig mg.
000	3·0, 3·0 } 3·0	0	3·1, 2·7 } 2·9	2	2·4, 2·8 } 2·6
00	2·8, 3·1 } 2·9	1	2·5, 2·7 } 2·6	3	2·5, 2·9 } 2·7

Series C.

Effect of time of immersion.

(Immersed area, 2·5 × 2·5 cms. Temp. 25·0° ± 0·1°.)

	Electrolytic iron, E 28.		Electrolytic zinc.	
Time, hrs.	M/10-KCl.	M/10-K_2SO_4.	M/10-KCl.	M/10-K_2SO_4.
1·5	0·4, 0·7 } 0·5	0·9, 0·6 } 0·7	1·6, 1·3 } 1·4	1·2, 2·1 } 1·6
4	1·1, 1·1 } 1·1	0·9, 1·1 } 1·0	3·1, 3·2 } 3·1	2·5, 2·8 } 2·6
7	1·9, 2·2 } 2·0	1·5, 2·1 } 1·8	6·5, 6·6 } 6·5	6·7, 5·5 } 6·1
14	3·6, 3·1 } 3·3	3·1, 3·2 } 3·1	9·8, 9·8 } 9·8	9·7, 9·0 } 9·3
24	4·8, 4·9 } 4·8	4·8, 4·9 } 4·8	15·0, 16·4 } 15·7	15·2, 15·8 } 15·5
48	9·1, 8·2 } 8·6	9·4, 10·3 } 9·8	29·2, 26·5 } 27·8	23·3, 27·9 } 25·6
70	13·0, 14·1 } 13·5	14·1, 13·1 } 13·6	34·6 *, 35·0 *	16·6 *, 21·0 *

Steel, H 28.

Time, hrs.	M/10-KCl.	M/10-NaCl.	M/10-K_2SO_4.	M/10-$MgSO_4$.
1·5	0·7, 0·6 } 0·6	0·7, 0·8 } 0·7	1·2, 0·6 } 0·9	0·4, 0·4 } 0·4
4	1·1, 1·0 } 1·0	—	1·2, 1·2 } 1·2	—
7	1·9, 2·2 } 2·0	2·0, 2·0 } 2·0	2·2, 2·8 } 2·5	0·6, 0·6 } 0·6
14	3·6, 3·6 } 3·6	—	3·5, 3·6 } 3·5	—
24	5·4, 5·5 } 5·4	4·4, 4·9 } 4·6	5·3, 6·1 } 5·7	1·0, 1·3 } 1·1
48	9·9, 11·1 } 10·5	12·2, 11·3 } 11·7	9·2, 9·9 } 9·5	3·0, 3·0 } 3·0
70	18·4, 16·8 } 17·6	14·4, 16·6 } 15·5	18·4, 16·8 } 17·6	—

* Results valueless owing to adherent matter (see p. 121).

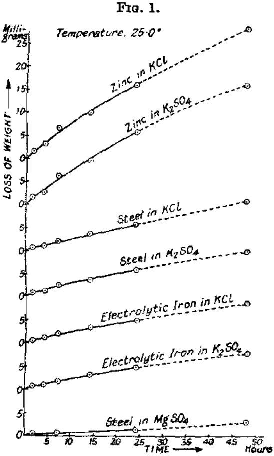
Discussion of Quantitative Results.

The experiments of Series A show that corrosion occurs more ıan twice as rapidly in oxygen as in air; since, however, the ›ecimens of sub-series (1) were necessarily exposed to air while eing placed in position, the ratio found for the two velocities ınnot be regarded as exact. The initial disturbance of the oxygen-‹posed specimens lasted for not more than 5% of the total time, ut it was decided to adopt air as the gaseous medium for the ›ries B and C. The effect of replacing air by oxygen is not only › increase the rate of corrosion, but also to restrict the corroded ›ea to strips running along the bottom portion and the two edges. his is an additional proof that the direct result of oxygen is the ›rmation of a protective film, and attack only occurs at places here the oxygen concentration is so low that it fails to keep the ›otective film in repair. The replacement of air by oxygen

multiplied the total corrosion by an amount varying from 2·4 to 2·6 in the different experiments; but owing to the greater localisation of attack, the *intensity* of corrosion (the corrosion per unit area of the part affected) was in several cases increased as much as 7 times.

The experiments of Series A also show that the effect of doubling the *breadth* of the specimens is nearly to double the corrosion, but the alternative method of increasing the immersed area, *viz.*, by prolonging the *depth* of the immersed portion, has much less effect. The effect of halving the concentration of potassium chloride is only slight.

FIG. 1.



The experiments of Series B were suggested by the qualitative observation that corrosion became visible earlier on finely ground than on coarsely ground specimens; these observations made it seem probable that whilst *local* abrasion of violent character increase corrosion of the part affected violent abrasion of the who surface somewhat retar attack by providing an u due number of weak point The results of Series showed, however, that eve after only 8 hours the effe of the character of abrasi had become trivial, although there appears to be a slight decrea of attack on passing from extremely fine to coarse abrasive.

Series C represents the main group of experiments, where t time of immersion was altered, the immersed area being ke constant. The data, plotted in Fig. 1, show that zinc is corrod much more rapidly than iron. On the other hand, steel giv curves almost parallel, in the early part, to those obtained w electrolytic iron. With zinc, steel, and electrolytic iron, potassi chloride yields curves nearly parallel to those obtained with pota ium sulphate; sodium chloride—in spite of rather irregular resu in the later stages—appears to cause an initial velocity of corros

similar to potassium chloride, but magnesium sulphate produces very much slower attack than potassium sulphate.

The interpretation of the experimental results is simple. The maximum available *E.M.F.* is that of the cells iron|oxygen or zinc|oxygen, but this will be in practice reduced by (*a*) *anodic polarisation*, (*b*) *cathodic polarisation*, and (*c*) *fall of potential across the liquid*. Where the conductivity of the liquid is very low, the factor (*c*) may be important, and here the conductivity may be the main factor in determining the rate of corrosion, as was found by Bengough, Stuart, and Lee for very dilute solutions in exceedingly pure water. For concentrated solutions, however, the fall of potential due to the resistance must certainly be very small, and the conductivity of the liquid, as such, will hardly affect the corrosion velocity; thus it is not surprising to find that the corrosion velocity is scarcely altered on passing from *M*/20- to *M*/10-potassium chloride. Probably on aluminium, where, owing to the self-healing character of the oxide skin, the anodic areas remain very small, the rate of corrosion is controlled mainly by factor (*a*); but on iron and zinc, where the anodic areas spread out over nearly the whole surface with great rapidity, it will be factor (*b*) which will determine the current passing between anodic and cathodic portions, *i.e.*, the rate of attack. The cathodic polarisation largely depends on the supply of oxygen (the "depolariser") to the portions bordering the water line. Thus pure oxygen causes more rapid corrosion than air, and the effect of doubling the *breadth* of the specimen is nearly to double the attack (it is not quite doubled, since there are exceptional opportunities for diffusion at the two ends of the water line). On the other hand, an increase of the vertical dimensions of the immersed area will not greatly affect the supply of oxygen, although it will increase the potential anodic area; thus the effect on the corrosion velocity is much less important. There is no reason why changing from potassium chloride to sodium chloride or to potassium sulphate should seriously affect the cathodic polarisation, and these changes hardly affect the corrosion velocity in the early stages, but the use of magnesium sulphate involves the deposition of a layer of sparingly soluble magnesium hydroxide over the cathodic region (clearly visible when the specimens are withdrawn), and this interferes with the diffusion of oxygen to the metallic surface, thus greatly retarding the attack.

There is no special reason why the presence of carbide in the metal should seriously affect the cathodic polarisation, and thus, in the early stages, steel corrodes with nearly the same velocity as iron. On the other hand, zinc corrodes with an entirely different velocity from iron, since here the *basic* value of the (unpolarised)

?.*M.F.* is different, and consequently, given the same facilities for xygen supply, the value of the current under polarisation conitions will be different for the two metals. Thus the partialmmersion method is capable of demonstrating differences between he corrosion resistance of different materials where such a difference xists, thus differing entirely from the total-immersion method, vhere—at great depths—the oxygen-supply rate might impress the ame velocity of corrosion on different metals.

In stating that steel corrodes at approximately the same rate as lectrolytic iron, it must be added that this applies only to conlitions of *differential* aeration, where an *E.M.F.* may be developed uite independently of the existence of a second phase in the metal. Under conditions of *uniform* aeration, the state of affairs is different. It was shown by the author (" Corrosion of Metals," 1926, p. 108) that, when discs of electrolytic iron were whirled in ordinary distilled water containing oxygen, practically no rusting occurred, although discs of steel whirled in the same water rapidly became rusty; where differential aeration currents are excluded, the *E.M.F.* between iron and carbide particles probably becomes important.

The fact that on ordinary iron and steel, chlorides and sulphates produce in the early stages approximately the same rate of corrosion, agrees with the results of former work with the drop method (*J. Soc. Chem. Ind.*, 1924, **43**, 315T). It is, of course, in contrast with the state of affairs met with in those materials where—owing to the highly protective quality of the oxide skin—the anodic areas remain small and the velocity is controlled by the anodic polarisation. Such an example is afforded by aluminium, where the penetrating chlorine ions produce much more rapid corrosion than sulphate ions, as is indicated by the long-period tests of Jablonski (*Korrosion u. Metallschutz*, 1926, **2**, 218).

In the later stages of corrosion, various complicating factors enter. The anodic area creeps up close to the water line, and the corrosion product begins to interfere perceptibly with access of oxygen to the metallic surface. Again, in some cases physical changes in the corrosion product may set in, increasing the error due to the matter which continues to adhere after wiping. Both these factors will tend to diminish the loss in weight. At the same time, other factors arise which tend to increase the rate of attack; for instance, alkali creeps up the surface above the water line, enlarging the potential cathodic area, at the expense, however, of increased circuit resistance. It would appear that the first set of factors predominates in the case of zinc, whilst in steel the second set is important, although the last part of the curve cannot be said to be definitely known, owing to lack of reproducibility. In any

case the change of weight measured in the later stages, although of technical importance, ceases to have any simple scientific significance.

It is to be noticed that in the early stages, where the anodic areas are small and anodic polarisation must be of perceptible influence, complete agreement between duplicates is not to be expected, since the number and distribution of weak points will vary from one specimen to another; actually at this early stage the divergence between the values given by duplicates often exceeds the balance error. Later, when the anodic areas grow, and cathodic polarisation controls the velocity, the agreement between duplicates in most cases becomes quite good. Moreover, almost the same results are given by different salts (potassium chloride and sulphate) and by different materials (electrolytic iron and steel); this fact is the more remarkable when we recall that the shapes, distribution, and aggregate areas of the anodic regions are utterly different in the various cases mentioned (for instance, the boundary of the anodic area is far more sinuous in chloride than in sulphate solutions). But when corrosion begins to develop from points close to the water line, the shutting off of oxygen may be different for the duplicate specimens, according to the chance disposition of the weak points relatively to the water line. Thus the agreement between duplicates becomes exceedingly poor.

Considering the question of reproducibility generally, it would seem that good agreement between duplicates may only be expected in certain circumstances, *viz.*, when the determining factor is *some external condition which can be controlled*; for instance, where it is determined by the supply of oxygen to an area which is clear of corrosion product, or where—as in Bengough's work on very dilute chloride solutions—it is determined by the concentration of chlorine ions. Reproducibility is definitely not to be expected, however, when the velocity is controlled by the chance distribution and sizes of a limited number of small anodic areas (weak spots). That the variation is not due to experimental error is proved by Bengough's work; here, in spite of extreme precautions, in a typical case the variation from the mean in two parallel experiments ranged from 1·7 to 6·7%. The difference of reproducibility under different conditions is also illustrated by the author's early work with the drop method (*J. Soc. Chem. Ind.*, 1924, **43**, 315T): four drops of N/10-potassium chloride, at 29·2°, gave practically the same amount of corrosion in 5·5 hours (*viz.*, 0·65, 0·65, 0·66, and 0·66 mg.), but in 48·7 hours the reproducibility had become poor (3·50, 2·57, 3·25, and 5·12 mg.), although clearly the effect of analytical error and initial disturbances (and indeed all *experimental* errors) must be

less serious in the longer experiments. Drops of potassium sulphate and nitrate gave similar results, but salts which can only succeed in penetrating exceptionally "weak" points showed far greater divergence between duplicates. Thus one drop of $M/30$-sodium phosphate produced 0·65 mg. of corrosion in 24 hours at 29·2°, whilst another drop of the same solution under identical conditions produced only 0·005 mg.; evidently the first drop happened to develop a weak spot, whilst the other did not. Many authorities appear to think that the study of "unreproducible phenomena" is unworthy of scientific attention. Where the divergence between duplicates is due to experimental error or lack of proper control this view is correct; but where the divergence is due to other causes, such an attitude is untenable. Clearly, however, it will be necessary, in studying cases (like corrosion by sodium phosphate) where results show variations over a wide range, to perform perhaps 10 or 20 repetitions of each experiment, and to use larger areas than are permitted by the drop method. The method described in this paper allows 15 experiments, each on an immersed area of 2·5 × 2·5 cms., to be performed simultaneously in a thermostat of ordinary laboratory size, and may prove useful for extending the work to such cases.

Summary.

The corrosion of half-immersed specimens of zinc, aluminium, iron, steel, and copper commences at certain weak points, mainly along the bottom and cut edges, but frequently in the centre also; in those cases where the rate of corrosion is very slow, it may occur along the water line. In zinc, iron, and steel in chloride or sulphate solutions, the attack spreads out from these points very rapidly, the greater part of the immersed area being finally attacked; the insoluble corrosion product is of four different types, which appear according to the manner in which the anodic and the cathodic products come together; in copper and aluminium one of these types is usually absent, but otherwise there is general correlation between the results with zinc, iron, and steel.

Quantitative experiments show that under conditions of differential aeration, electrolytic iron is attacked nearly as rapidly as steel, and potassium sulphate and potassium chloride cause similar rates of corrosion, notwithstanding that the shapes of the corroded area are quite different; magnesium sulphate causes much slower attack. Zinc is attacked more quickly than iron, and aluminium much more slowly. Oxygen produces quicker attack on steel than air, but the attack is restricted to a smaller portion of the specimens; doubling the breadth of half-immersed specimens nearly doubles the rate of attack, but increase of the length of the immersed area

has much less effect. All these results are understood if it is remembered that the corrosion current flowing between the cathodic and the anodic areas will depend on the *E.M.F.* of the cell metal|oxygen greatly reduced by polarisation. With aluminium, where the film repairs itself readily and the anodic areas remain small, the anodic polarisation will be most important, but with zinc, iron, and steel, the cathodic polarisation, which depends on the supply of oxygen, will determine the rate of attack; iron is corroded less quickly by magnesium sulphate than by potassium sulphate, since the cathodic product, magnesium hydroxide, interferes with the access of oxygen to the metal; zinc is corroded more quickly than iron—even with the same facilities of oxygen supply—because here the value of the unpolarised *E.M.F.* is higher.

[*Received, November 3rd*, 1928.]

XVIII.—*The Partial Esterification of Polyhydric Alcohols. Part VII. The Unreliability of Proofs of the Structure of Disubstituted Glycerols.*

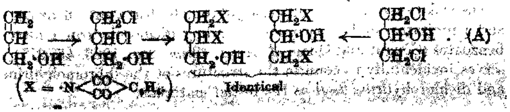
By Arthur Fairbourne and Geoffrey Wilson Cowdrey.

It was previously shown (Part V, J., 1926, 3148; *Ann. Reports*, 1927, 90) that the alleged structures of "β"-monoglycerides were untrustworthy.

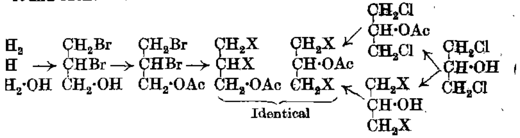
Several "αβ"-disubstituted glycerols have now been prepared, and found identical with their "αγ"-isomerides.

Philippi and Seka (*Annalen*, 1923, **433**, 88) obtained the "αβ"-diphthalimido-derivative from αβ-dibromohydrin and converted it into a diamine apparently identical with the necessarily unsymmetrical or αβ-diamine resolved by Abderhalden and Eichwald (*Ber.*, 1916, **49**, 2095), and also into other derivatives showing independent evidence of structure.

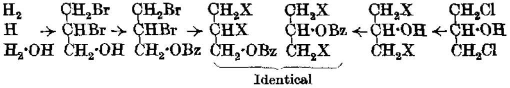
The present authors have repeated this preparation, and have shown by the mixed melting point method that the product is identical with the "αγ"-isomeride as prepared by Gabriel (*Ber.*, 1889, **22**, 224. Compare also Gödeckmeyer, *Ber.*, 1888, **21**, 2684).



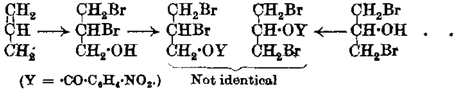
Their *monoacetates* have also been independently prepared and found identical.



The corresponding *benzoates* have similarly been synthesised, each by methods often regarded as sufficient proofs of structure, and they too are identical.

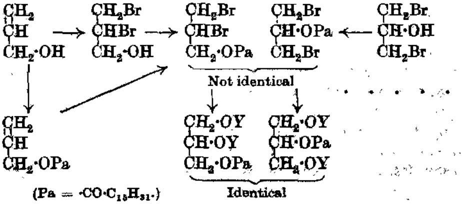


On the other hand, *different* dibromohydrin *p*-nitrobenzoates hav been obtained (Part V, *loc. cit.*).



(D)

A similar series of syntheses has now also produced differen *dibromohydrin palmitates*, but these react to produce identica *di*-p-*nitrobenzoates*.



(E)

The isolation of the two different dibromohydrin *p*-nitrobenzoate and palmitates, and of two corresponding dichlorohydrin *p*-nitro benzoates (Conant and Quayle, *J. Amer. Chem. Soc.*, 1923, **45**, 2771 serves incidentally to confirm the structures of the dibromohydrin and dichlorohydrins used as the initial materials.

Several similar cases of structural confusion in compounds of the glycerol type occur in the literature, and various explanations have been put forward to account for them. For instance, Gabriel and Ohle (*Ber.*, 1917, **50**, 804) found that β-chloro-*n*-propyl alcohol was converted into phthalimido*iso*propyl alcohol (F) by potassium phthalimide, and that the acetate (G) behaved similarly.

$$\begin{array}{lcl} CH_3 & & CH_3 \\ CHCl & \longrightarrow & CH{\cdot}OH \text{ (or OAc)} \\ CH_2{\cdot}OH \text{ (or OAc)} & & CH_2X \end{array} \quad . \quad . \quad (F), (G)$$

They suggest that these results may be due to the formation of propylene oxide through loss of hydrogen chloride, either during the reaction in case (F), or previously, with the production of an impure initial material, in case (G). Their explanation can easily be extended to apply to the partial substitutions of glycerol by regarding epichlorohydrin as the corresponding ethylene oxide (compare Gödeckmeyer, *loc. cit.*), an hypothesis put forward by Boyd (J., 1901, **79**, 1221) to account for his obtaining identical diphenyl ethers from αβ-dibromohydrin and αγ-dichlorohydrin.

$$\begin{array}{lclclclcl} CH & & CH_2Br & & CH_2{\cdot}OPh & & CH_2{\cdot}OPh & & CH_2Cl \\ CH & \longrightarrow & CHBr & \longrightarrow & CH{\cdot}OPh & & CH{\cdot}OH & \longleftarrow & CH{\cdot}OH \\ CH_2{\cdot}OH & & CH_2{\cdot}OH & & CH_2{\cdot}OH & & CH_2{\cdot}OPh & & CH_2Cl \end{array} \quad . \quad . \quad (H)$$

Identical

On the other hand, the hypothesis cannot explain, for example, the formation of the identical *p*-nitrobenzoates in (E).

Moreover, Fischer (*Ber.*, 1920, **53**, 1621) has studied reactions where this explanation seems untenable. "αβ"-Diacyliodohydrins were found to be convenient initial materials for the preparation of "αγ"-compounds. Triglycerides were then synthesised from these.

$$\begin{array}{lclclclcl} CH_2{\cdot}OH & & CH_2{\cdot}OZ & & CH_2{\cdot}OZ & & CH_2{\cdot}OZ & CH_2{\cdot}OZ & & CH_2{\cdot}OH \\ CH{\cdot}OH & \rightarrow & CH{\cdot}OZ & \rightarrow & CH{\cdot}OZ & \rightarrow & CH{\cdot}OZ & CH{\cdot}OZ & \leftarrow & CH{\cdot}OH \\ CH_2I & & CH_2I & & CH_2{\cdot}OH & & CH_2{\cdot}OZ' & CH_2{\cdot}OZ' & & CH_2{\cdot}OZ' \end{array} \quad (I)$$

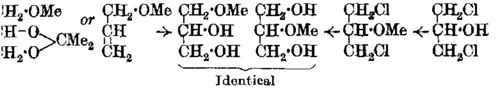
(Z = ·COR ; Z′ = ·COR′.) Not identical

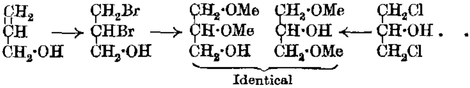
He thought that conversion probably occurred during the removal of the iodine, and involved the formation of a complex intermediate of the ortho-ester type—a suggestion not dissimilar from that of Grün (*Ber.*, 1921, **54**, 290), who held that both the wandering of acyl groups in glycerides generally and also the curious phenomenon of double melting points shown by certain glycerides, including tristearin, are due to the two forms of the carboxyl group identified by Hantzsch (*Ber.*, 1917, **50**, 1422). It is noteworthy in this

connexion that the two solvents which cause alternation of melting point of glyceryl tribenzoate (J., 1925, **127**, 2759) are actually those by which Hantzsch obtained different absorption spectra.

Nevertheless, no such explanation can account for (A) and (F) above, or for (J), (K), and (M) below.

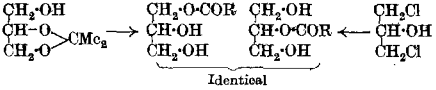
Gilchrist and Purves (J., 1925, **127**, 2735) prepared the "α"-monomethyl ether and the "αβ"-dimethyl ether of glycerol, and proved identity in each case with the supposed isomeride by methods other than that of "mixed melting point."

 (J)

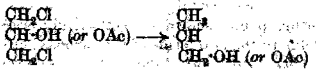
 . . (K)

Their suggestion that the conversions might be due to unsatisfactory αγ-dichlorohydrin is negatived by the experiment of Conant and Quale (*loc. cit.*).

Two exactly similar cases to (J), but each involving esters instead of ethers, were recorded previously (Part V, *loc. cit.*), and it may be added that no water was introduced during the reactions.

 . (L)

Allyl alcohol, which enters directly or indirectly into most of the synthetic proofs of "αβ"-disubstitution (compare the above reactions; J., 1921, **119**, 1035; 1926, 3146; Part V, *loc. cit.*; and also particularly Irvine, Soutar, and Macdonald, J., 1915, **107**, 337; Fischer, Bergmann, and Bärwind, *Ber.*, 1920, **53**, 1589; Fischer and Pfähler, *ibid.*, p. 1606), can itself be produced from αγ-dichlorohydrin by means of sodium (Lourenço, *Ann. Chim.*, 1863, **67**, 323) (M), and its acetate may be produced in a similar way (Bigot, *ibid.*, 1891, **22**, 433) (N).

 (M), (N)

αβ-Dibromohydrin reacts similarly with sodium (Aschan, *Ber.*, 1890, **23**, 1831).

No explanation, common to all these very similar conversions, having been advanced, it is considered that the only absolute proof of unsymmetrical structure in disubstituted glycerols is resolution into optically active forms (Abderhalden and Eichwald, *Ber.*, 1914, **47**, 1856, 2880; 1915, **48**, 1847; *loc. cit.*; Bergmann and co-workers, *Ber.*, 1921, **54**, 936; *Z. physiol. Chem.*, 1924, **137**, 27, 47); and that even this proof cannot normally be regarded as extending with any certainty to derivatives.

When direct rotatory evidence is not available, and until the matter is better understood, it would seem reasonable, therefore, (a) *when a disubstituted glycerol exists as two isomerides*, to assume, in the absence of proof to the contrary, that these have the structures of their respective parent substances, or derivatives; and (b) *in all other cases*, to appreciate that conversion may have occurred. Such conversions are usually supposed to lead preferentially to αγ-disubstituted glycerols, but, in any case, the structures recorded, for example, by Gilchrist and Purves (*loc. cit.*) for glycerol dimethyl ether and for glycerol glucoside must clearly be regarded as unproven. The significance of these difficulties in relation to work on the higher polyhydric alcohols generally will be appreciated.

EXPERIMENTAL.

Diphthalimidohydroxypropane (A).—Specimens prepared by the methods of Philippi and Seka (*loc. cit.*) and of Gabriel (*loc. cit.*) for synthesising the "αβ"- and the "αγ"-diphthalimide, respectively, melted, alone or mixed, at 204°. The supposed isomerides are therefore identical.

Diphthalimidoacetoxypropane (B).—(*a*) A mixture of αβ-dibromohydrin (1 mol.) and acetyl chloride (1·5 mols.) was refluxed for ½ hour; the excess of the latter was then removed under reduced pressure. The "αβ"-dibromomonoacetin distilled at 227—228° (compare Aschan, *Ber.*, 1890, **23**, 1826).

3·6 G. of this product were intimately mixed with 5 g. of potassium phthalimide and heated, first at 140°, and later at 160—170° for ½ hour. The cooled product was extracted with glacial acetic acid; the *acetate* obtained, after being washed with alcohol and ether, melted at 194° (Found: C, 64·6; H, 4·5; *M*, ebullioscopic in acetone, 428. $C_{21}H_{16}O_6N_2$ requires C, 64·3; H, 4·1%; *M*, 392). The structure of this substance is discussed in the theoretical section (compare Philippi and Seka, *loc. cit.*, who prepared probably the same compound from allyl acetate).

(*b*) 3 G. of "αγ"-dichloromonoacetin, b. p. 202—208°, prepared

from *αγ*-dichlorohydrin by Henry's method (*Ber.*, 1871, 4, 701), was intimately mixed with 6·5 g. of potassium phthalimide and heated at 150—170° for ½ hour. The product, treated in the manner described above, gave an acetate which, alone or mixed with that obtained as in (*a*), melted at 194°.

(*c*) A mixture of 0·5 g. of "*αγ*"-diphthalimidohydroxypropane (Gabriel, *loc. cit.*) and 3 c.c. of acetyl chloride was refluxed for 10 minutes and then poured into ice-water. The acetate, isolated and purified as described above, melted at 194°, alone or mixed with that obtained as in (*a*) or as in (*b*).

Diphthalimidobenzoyloxypropane (C).—(*a*) 6·4 G. of dibromohydrin monobenzoate, prepared in a similar manner as the above dibromohydrin monoacetate, from αβ-dibromohydrin (compare Philippi and Seka, *loc. cit.*), and 7·4 g. of potassium phthalimide were intimately mixed and heated at 170° for ½ hour, liquefaction occurring. The mass was extracted with glacial acetic acid, and the *benzoate* crystallised from the extract in colourless prisms, m. p. 194—195° (Found: C, 68·9; H, 4·1. $C_{26}H_{18}O_6N_2$ requires C, 68·7; H, 3·9%).

(*b*) An attempt to prepare the compound from "*αγ*"-dichlorohydrin monobenzoate was not successful. 0·5 G. of the "*αγ*"-diphthalimide described above was therefore dissolved in 2 c.c. of benzoyl chloride and warmed on a water-bath for ½ hour, the excess of benzoyl chloride then being destroyed by means of warm water and dilute sodium carbonate solution. The residual solid, after crystallising from chloroform–alcohol, had m. p. 195°, alone or mixed with the benzoate obtained as in (*a*). (A mixture with the corresponding acetoxy-compound, which has nearly the same melting point, melted indefinitely at about 175°.)

Allyl Palmitate, $C_{15}H_{31}{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2$.—13·5 G. of palmitic acid and 27 c.c. of thionyl chloride were warmed at 60° for an hour, the excess of the latter was distilled under reduced pressure, 4 c.c. of allyl alcohol were added, and the mixture was refluxed on a water-bath for 90 minutes. After removal of the unchanged allyl alcohol under diminished pressure, the residue was extracted in ether, shaken with water, dilute sodium bicarbonate solution, and again with water, dried over sodium sulphate, and boiled with charcoal. The light brown oil finally obtained solidified in ice; m. p. 20—25°. The quantity was not sufficient for final purification or combustion, but the ester brominated to produce *αβ-dibromohydrin palmitate* which, alone or mixed with a specimen obtained as described immediately below, melted at 34°.

αβ-Dibromohydrin Palmitate, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{15}H_{31}$.—The details of the preceding preparation and purification were followed almost exactly, 12·9 g. of αβ-dibromohydrin being used

in place of 4 c.c. of allyl alcohol. The product crystallised from alcohol in colourless needles, m. p. 34° (Found: C, 49·9; H, 7·9; Br, 35·0. $C_{19}H_{36}O_2Br_2$ requires C, 50·0; H, 7·9; Br, 35·1%).

The reason for assigning the αβ-formula to this isomeride is discussed at the end of the theoretical section.

αγ-Dibromohydrin palmitate, $C_{15}H_{31}\cdot CO\cdot O\cdot CH(CH_2Br)_2$, m. p. 35·5°, was obtained in the same way as the αβ-compound, 7·3 g. of palmitic acid, 15·2 c.c. of thionyl chloride, and 6·5 g. of αγ-dibromohydrin being used (Found: Br, 34·7%). Mixed with the αβ-isomeride, it melted at about 28°. Attempts to act upon either isomeride with potassium phthalimide were not successful.

Monopalmitin Di-p-*nitrobenzoate* (E).—(*a*) 1·1 G. of silver *p*-nitrobenzoate and 5·8 g. of αβ-dibromohydrin palmitate were intimately mixed with the aid of dry ether and heated to 150°; partial liquefaction then occurred. The mixture was maintained at 130—140° for 3 hours with frequent stirring, cooled, and extracted with chloroform. The extract was boiled with charcoal and caused to crystallise by the addition of alcohol. Recrystallisation from chloroform–alcohol yielded colourless needles, m. p. 102° (Found: C, 62·7; H, 6·9; *M*, cryoscopic in benzene, 625. $C_{33}H_{44}O_{10}N_2$ requires C, 63·1; H, 7·0%; *M*, 628).

(*b*) An exactly similar preparation carried out with αγ- instead of αβ-dibromohydrin palmitate gave the same product, m. p. 102°, and mixed m. p. 102°.

αγ-Dichlorohydrin Triphenylmethyl Ether,

$$CH_2Cl\cdot CH(O\cdot CPh_3)\cdot CH_2Cl.$$

—A solution of 10 g. of triphenylmethyl chloride and 4 c.c. of αγ-dichlorohydrin in 25 c.c. of pyridine was kept at 100° for 2 hours, allowed to stand for 12 hours, and then poured into 100 c.c. of water. The product, which solidified during ½ hour, was ground with water and extracted with ether. The *ether* isolated from the extract, after crystallising several times from alcohol, melted at 108—109°, was stable to aqueous potash, and did not react with potassium phthalimide (Found: Cl, 19·5. $C_{22}H_{20}OCl_2$ requires Cl, 19·1%). That it possesses the β-triphenylmethyl structure is probable from the work of Helferich and Sieber (*Z. physiol. Chem.*, 1927, **170**, 31).

The authors wish to express their indebtedness to the Chemical Society for a grant which has partly met the expenses incurred in this work.

KING'S COLLEGE, LONDON. [*Received, August 30th, 1928.*]

XIX.—*Studies in the Phenylsuccinic Acid Series. Part IX. The Resolution of* r-*Diphenylsuccin-α- and -β-naphthylamic Acids into their Optical Antipodes.*

By Henry Wren and Edward Wright.

In continuation of the work of Wren and Burrows (J., 1924, **125**, 1934), the resolution of *r*-diphenylsuccin-α- and -β-naphthylamic acids has been effected by the alkaloidal method. The active acids, like the corresponding anilic and *p*-toluidic acids (*loc. cit.*), exhibit the high optical activity characteristic of simple derivatives of the active diphenylsuccinic acids. Conversion of the acids into the substituted imides is accompanied by very marked diminution in specific rotation, the optical effect of the change thus resembling that of the transformation of the active diphenylsuccinic acids into their anhydrides (Wren and Still, J., 1915, **107**, 1457). The influence of the aryl group on the specific rotation of the substituted diphenylsuccinamic acids and the diphenylsuccinimides appears quite irregular; for the former group the substituents fall into the descending sequence β-naphthyl, phenyl, *p*-tolyl, α-naphthyl, whereas for the latter group the order is α-naphthyl, *p*-tolyl, phenyl, β-naphthyl.

Experimental.

Resolution of r-*Diphenylsuccin-α-naphthylamic Acid into its Optical Antipodes.*—r-*Diphenylsuccin-α-naphthylamic acid*, m. p. 217—219° (decomp.), was prepared by mixing solutions of equivalent quantities of *r*-diphenylsuccinic anhydride and α-naphthylamine in cold benzene and purified by crystallisation from rectified spirit (Found: C, 79·0; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%).

A solution of *r*-diphenylsuccin-α-naphthylamic acid (25·1 g.) and quinine (24·1 g.) in boiling absolute ethyl alcohol (175 c.c.) was filtered and preserved in an ice-chest during 3 days. The ill-defined crystals which separated (26·5 g.) were crystallised repeatedly from the same solvent, 5 c.c. of the latter being used for each gram of material. The course of the resolution was followed by observing the specific rotations in acetone of the acids isolated from the successive filtrates, the following values being obtained: − 155·5°, − 61·4°, + 93·4°, and + 154·9°. The residual quinine salt (9·6 g.) was decomposed with dilute sulphuric acid and ether, and the crude d-*diphenylsuccin-α-naphthylamic acid* crystallised from 80% alcohol until its specific rotation remained constant. It formed small needles, m. p. 206—207° (Found: C, 78·8; H, 5·4%). In acetone (l = 2, c = 0·8432) $\alpha_D^{18°}$ + 3·47°, whence $[\alpha]_D^{18°}$ +205·8°.

l-Diphenylsuccin-α-naphthylamic acid ($[\alpha]_D$ − 123·2° in acetone;

16·7 g.), from the crude lævorotatory mixture of acids obtained from the first filtrates of the quinine salt (see above), and cinchonidine (13 g.) were dissolved in boiling ethyl alcohol (120 c.c.). The salt, which separated very slowly from the cold solution, was recrystallised from alcohol and decomposed in the usual manner, yielding l-*diphenylsuccin-α-naphthylamic acid* having $[\alpha]_D$ − 194·3° in acetone. Crystallisation of the crude acid from 80% alcohol afforded the homogeneous acid, which exactly resembled its optical antipode in appearance, solubility and melting point. It had $[\alpha]_D^{17°}$ − 206·6° in acetone solution ($l = 2$, $c = 0·9484$, $\alpha_D^{17°}$ − 3·92°) (Found : C, 79·2; H, 5·4%).

d-*Diphenylsuccin-α-naphthil*, m. p. 145°, was prepared by the action of boiling ethyl-alcoholic hydrogen chloride (3%) on the corresponding acid. The crude product had $[\alpha]_D$ + 136·8° in acetone, thus showing that appreciable racemisation had not occurred during the course of the change. After crystallisation from absolute alcohol containing a little hydrogen chloride, the compound was optically homogeneous. In acetone ($l = 2$, $c = 1·0916$) $\alpha_D^{16°}$ + 3·04°, whence $[\alpha]_D^{16°}$ + 139·2°; in chloroform ($l = 2$, $c = 1·2608$), $\alpha_D^{17°}$ + 3·11°, whence $[\alpha]_D^{17°}$ + 123·3° (Found : C, 82·9; H, 5·2. $C_{26}H_{19}O_2N$ requires C, 82·7; H, 5·1%).

d-Diphenylsuccin-α-naphthil is unusually readily racemised by sodium ethoxide in alcoholic solution. Crystallisation of the active material from boiling alcohol was occasionally accompanied by complete racemisation. The danger was avoided by the use of alcohol containing a trace of hydrogen chloride.

Resolution of r-*Diphenylsuccin-β-naphthylamic Acid into its Optical Antipodes.*—*r*-Diphenylsuccin-β-naphthylamic acid (m. p. 201—202°; prepared in almost quantitative yield in the same manner as the α-acid and purified by crystallisation from rectified spirit) (49·8 g.) and quinine (23·6 g.) were dissolved in boiling absolute alcohol and the solution was preserved in an ice-chest during 3 days. The needles (27·8 g.) which slowly separated were repeatedly crystallised from the same solvent, 20 c.c. of which were used for each gram of salt. The acid recovered from the successive filtrates had $[\alpha]_D$ − 96·3°, − 56·4°, + 44·0°, + 126·2° and + 210°, respectively, in acetone. The crude dextrorotatory acid isolated from the residual salt was crystallised from 80% alcohol until successive crops had a constant specific rotation. d-*Diphenylsuccin-β-naphthylamic acid* crystallises in small needles, m. p. 188° (Found : C, 78·8; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%). In acetone ($l = 2$, $c = 0·7288$) $\alpha_D^{15·5°}$ + 5·64°, whence $[\alpha]_D^{15·5°}$ + 386·9°.

Preparation of the homogeneous l-acid from the crude lævorotatory mixture of acids isolated from the initial filtrates obtained in

the foregoing resolution could not be effected by crystallisation or by means of cinchonine, cinchonidine, or brucine.

d-*Diphenylsuccin*-β-*naphthil*, prepared in the same manner as the α-compound, separated from alcohol, containing a trace of hydrogen chloride, in slender needles, m. p. 178—179° (Found: C, 82·9; H, 5·1. $C_{26}H_{19}O_2N$ requires C, 82·7; H, 5·1%). In acetone ($l = 2$, $c = 0{\cdot}8792$) $\alpha_D^{18°}$ + 1·845°, whence $[\alpha]_D^{18°}$ + 104·9°.

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XX.—*Studies in the Phenylsuccinic Acid Series. Part X. Racemisation Phenomena observed during the Action of Water and Bases on the Optically Active Diphenylsuccinic Anhydrides.*

By HENRY WREN and EDWARD WRIGHT.

THE optically active diphenylsuccinic anhydrides are converted by hot water into diphenylsuccinic acids of similar sign which contain about 8% of optically inactive material from which *meso*diphenylsuccinic acid can be isolated in small amount (Wren and Still, J., 1915, **107**, 1451). With cold ethyl alcohol and the *l*-anhydride a rather more complex result is obtained, the product containing about 20% of optically inactive material consisting, in part at any rate, of ethyl hydrogen *r*- and *meso*-diphenylsuccinates (*loc. cit.*; also Wren and Williams, J., 1918, **113**, 832). The greater extent of the racemisation under the milder experimental conditions appeared to indicate a profound influence of the particular reagent effecting the opening of the diphenylsuccinic anhydride ring and has led to the further observation of the behaviour of water and bases under varied conditions. The production of substituted amic acids from the active anhydrides and aniline, *p*-toluidine, α- or β-naphthylamine in presence of cold benzene is accompanied by not more than slight, if any, racemisation; it may be noted that Wren and Williams (*loc. cit.*) failed to find any evidence of the production of *meso*-forms when the *r*-anhydride reacted with amines. On the other hand, the optical activity of the diphenylsuccinic acids resulting from the action of water on the active diphenylsuccinic anhydrides is influ-

enced in an extraordinary degree by the presence of a mutual solvent. Homogeneous *d*-diphenylsuccinic acid has $[\alpha]_D^{17°}$ + 397·3° in acetone (Wren and Still, J., 1915, **107**, 449). The acid produced from the *l*-anhydride and aqueous acetic acid is only slightly racemised. In ether saturated with water the *d*-anhydride yields an acid having $[\alpha]_D$ + 232·7° (in acetone), whereas in aqueous acetone and pyridine the activity of the acid falls to + 116·5° and + 22·4° respectively. Determination of the proportion of *meso*diphenylsuccinic acid in the products has been effected according to the method of Anschütz and Bendix (*Annalen*, 1890, **259**, 81), which depends on the widely differing solubilities of barium *r*- and *meso*-diphenylsuccinates in water; the presence of optically active acid in the product is without influence on the analytical procedure, since the solubilities of the barium salts of the racemic and the active acids are closely similar (compare J., 1915, **107**, 1449). In every case the production of a small proportion of the *meso*-acid has been established. Since a high degree of accuracy could scarcely be expected with the small amounts of material available from the active anhydrides, control experiments have been performed with larger quantities of the more accessible *r*-anhydride under identical conditions. The fundamental assumption that the latter substance in dilute solution behaves as a mixture of the *d*- and *l*-forms is not, however, universally true. In aqueous ether, acetone, and pyridine the results afforded by the two sets of data are reasonably concordant. In aqueous acetic acid, on the other hand, the product obtained from the *r*-anhydride contains somewhat more than 20% of the *meso*-acid, whereas the *l*-acid derived from the *l*-anhydride contains about 6% of optically inactive material.

EXPERIMENTAL.

The *d*- and *l*-diphenylsuccinic anhydrides, prepared according to the method of Wren and Still (J., 1915, **107**, 1449), had $[\alpha]_D^{14°}$ + 278·8° and $[\alpha]_D$ − 286·5° in benzene.

Interaction of Amines and Optically Active Diphenylsuccinic Anhydrides.—(a) *α-Naphthylamine.* α-Naphthylamine (0·5482 g.), dissolved in benzene, was mixed with *l*-diphenylsuccinic anhydride (0·966 g.) in benzene solution. Reaction was complete within a few minutes, after which the solvent was removed at atmospheric temperature and the residual solid dried in a vacuum until constant in weight. The product obtained had $[\alpha]_D^{19.5°}$ − 200·3° in acetone (l = 2, c = 0·9412, $\alpha_D^{19.5°}$ − 3·77°). Crystallisation of it from 80% alcohol gave homogeneous *l*-diphenylsuccin-α-naphthylamic acid, m. p. 206—207°, $[\alpha]_D^{16°}$ − 207·3° in acetone (compare Wren and Wright, preceding paper).

(b) β-*Naphthylamine*. β-Naphthylamine (0·5229 g.) was treated with the equivalent amount of *l*-diphenylsuccinic anhydride in benzene, the same procedure being adopted as with the α-amine. The crude acid had $[\alpha]_D^{19°}$ − 378·8° in acetone (l = 2, c = 0·8248, $\alpha_D^{19°}$ − 6·25°). Purification of the product from 80% alcohol gave l-*diphenylsuccin*-β-*naphthylamic acid*, which crystallised in small needles, m. p. 188—188·5° (Found: C, 79·0; H, 5·4. $C_{26}H_{21}O_3N$ requires C, 79·0; H, 5·4%). In acetone solution (l = 2, c = 0·7355) $\alpha_D^{17·5°}$ − 5·72°, whence $[\alpha]_D^{17·5°}$ − 388·2°. For *d*-diphenylsuccin-β-naphthylamic acid the m. p. 188° and $[\alpha]_D^{16·5°}$ + 386·9° (in acetone) are recorded hy Wren and Wright (*loc. cit.*).

(c) *Aniline*. Freshly distilled aniline (0·429 g.) and the equivalent amount of the *l*-anhydride in benzene yielded *l*-diphenylsuccinanilic acid having $[\alpha]_D^{19°}$ − 325·0° in acetone (l = 2, c = 0·8070, $\alpha_D^{19°}$ − 5·24°), whereas Wren and Burrows (J., 1924, **125**, 1934) record $[\alpha]_D^{19·2°}$ − 338·2° for the homogeneous acid.

(d) p-*Toluidine*. The *l*-diphenylsuccino-*p*-toluidic acid derived from 0·3433 g. of *p*-toluidine had $[\alpha]_D$ − 319·5° in acetone (l = 2, c = 0·8544, α_D − 5·46°); the homogeneous acid has $[\alpha]_D^{18·8°}$ − 329·5° in the same solvent (Wren and Burrows, *loc. cit.*).

Interaction of Water and Optically Active Diphenylsuccinic Anhydrides in the Presence of Solvents.—(a) *Acetone*. A solution of *d*-diphenylsuccinic anhydride (0·7742 g.) in a mixture of acetone (20 c.c.) and water (5 c.c.) was preserved at laboratory temperature during 3 days. It was then allowed to evaporate spontaneously and the residue was dried in a vacuum desiccator until constant in weight. It had $[\alpha]_D^{17°}$ + 116·7° in acetone (l = 2, c = 0·9425, $\alpha_D^{17°}$ + 2·20°), whereas the homogeneous acid has $[\alpha]_D^{17°}$ + 393·3°. The proportion of *meso*-acid in the product was 4·5%.

(b) *Pyridine*. The *d*-anhydride (1·1974 g.) was preserved in a solution of pyridine (24 c.c.) and water (6 c.c.) during 3 days. The mixture was treated with an excess of dilute hydrochloric acid, and the diphenylsuccinic acid removed by ether. In acetone, it had $[\alpha]_D^{17°}$ + 22·4° (l = 2, c = 0·8488, $\alpha_D^{17°}$ + 0·38°); it contained 3·4% of *meso*-acid. Repetition of the experiment gave an acid with $[\alpha]_D$ + 21·1° in acetone.

(c) *Ether*. The *d*-anhydride (0·8336 g.) was dissolved in 30 c.c. of ether saturated with water; 4 c.c. of water were added, after which the solution was preserved at atmospheric temperature during 3 days. The *d*-acid obtained had $[\alpha]_D$ + 232·7° in acetone (l = 2, c = 0·9260, α_D + 4·31°) and contained 2·8% of the *meso*-form.

(d) *Acetic acid*. The *l*-anhydride (0·9995 g.) was preserved in

85% acetic acid (35 c.c.) during 3 days. The bulk of the acetic acid was removed by distillation under diminished pressure below 40° and the remainder in a vacuum over soda-lime. The isolated *l*-diphenylsuccinic acid had $[\alpha]_D^{19.5°}$ − 364·7° in acetone (l = 2, c = 0·8828, $\alpha_D^{19.5°}$ − 6·44°) and contained 3·6% of the *meso*-form. A second experiment gave an acid with $[\alpha]_D$ − 373·3° in acetone.

Interaction of Water and r-*Diphenylsuccinic Anhydride in the Presence of Solvents.*—The experiments were performed in exactly the same manner as the corresponding ones with the active anhydrides except that much larger quantities were employed. The percentage of *meso*-acid in the mixed acids obtained by use of aqueous acetone, pyridine, and ether was 2·0, 2·0, and 1·0 respectively. With acetic acid, however, the values 21·6, 22·3, and 20·6 were found in three successive experiments.

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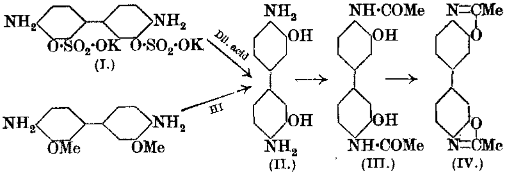
XXI.—*Nitroarylsulphuric Acids and their Reduction Products.*

By GEORGE NORMAN BURKHARDT and HAROLD WOOD.

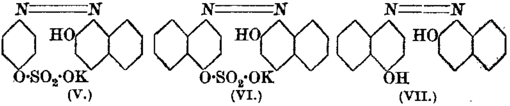
THE method of preparing arylsulphuric acids by the addition of a phenol or naphthol to dimethylaniline chlorosulphonate in carbon disulphide (Burkhardt and Lapworth, J., 1926, 684) has been applied satisfactorily to *o*-, *m*-, and *p*-nitrophenols and to 4-nitro-1-naphthol and 1-nitro-2-naphthol, but only small amounts of the sulphuric ester were formed from 2-nitro-1-naphthol. The potassium salts which were isolated were remarkably stable for derivatives of such acid-phenols and were reduced by ferrous hydroxide to amino-compounds, which gave acetyl and benzylidene derivatives without losing the sulphate group. Potassium *o*-nitrophenyl sulphate was reduced in alkaline solution to the azo- and hydrazo-derivatives and converted into *potassium* 4 : 4′-*diaminodiphenylene* 3 : 3′-*disulphate* (I; yield, 50%). The constitution of the last compound was confirmed by hydrolysing it with boiling dilute hydrochloric acid and comparing the dihydroxybenzidine produced with that obtained by demethylating dianisidine with hydriodic

acid (compare German Pat. 70718). The dihydroxybenzidine (II) was characterised by means of the *dianhydrodiacetyl* derivative (IV).



During the diazotisation of aminoaryl sulphates under ordinary conditions the sulphate group was removed whenever it was in the *o*-position to the amino-group. However, whereas 1-amino-2-naphthol in diazotisation gives β-naphthaquinone (Grandmougin and Michel, *Ber.*, 1892, **25**, 972), the sulphuric ester gives the diazo-oxide, indicating that some protective effect is operating even in this case. This splitting off of substituents during diazotisation has many well-known analogies, but displacements are rare in monosubstituted amines.

The aminoaryl sulphates with the amino- and sulphato-groups in the *m*- or *p*-position diazotised normally and the diazo-derivatives coupled with β-naphthol to give azo-compounds containing the sulphato-group, which makes them soluble acid dyes (*e.g.*, V and VI, comparable with Orange II and Fast Red A respectively).



Attempts were made to dye wool and silk with these and subsequently to hydrolyse the dye on the fibre to relatively insoluble products (*e.g.*, VII). The hydrolysis on the fibre was found to be more difficult than in aqueous solution, as Green also observed with the ionamines, and dull shades were produced when such hydrolysis was brought about by heating with 1% sulphuric acid, a much greater strength than is normally used in dyeing operations. Further, the hydroxyazo-dyes, which were insoluble in water, were stripped by soap, as was to be expected with *p*-hydroxyazo-dyes of low molecular weight.

The isomeric 2- and 4-nitro-1-naphthols were separated nearly quantitatively by forming the potassium salts in aqueous alcohol.

Experimental.

Preparation of Nitronaphthols.—1-*Nitro-2-naphthol.* Aceto-β-naphthalide was nitrated by Friedländer and Littner's method (*Ber.*, 1915, **48**, 330). The product which crystallised from the benzene extract (yield, 60%) was refluxed for 2 hours with alcohol (2½ vols.) and 50% aqueous potassium hydroxide (1 vol.). The residue after evaporation of the alcohol was twice recrystallised from boiling water, and an aqueous solution acidified to give pure 1-nitro-2-naphthol.

2- *and* 4-*Nitro*-1-*naphthols.* α-Naphthylamine (30 g.) was boiled for 5 minutes with glacial acetic acid (200 c.c.) and acetic anhydride (27 c.c.) (Hodgson and Kilner, J., 1924, **125**, 807), and nitric acid (12·5 c.c.; *d* 1·5) added to the suspension resulting on cooling to 20—25°. After 2 days the solid (30 g.) was filtered off, washed twice with glacial acetic acid, and heated with alcohol (90 c.c.), aqueous caustic potash (60 c.c. of 30%) and water (100 c.c.) were added, and the alcohol was distilled off slowly. When 70 c.c. had distilled, more water (100 c.c.) was added and the distillation continued on a sand-bath until the distillate was free from ammonia (total time, 3½ hours). The potassium 2-nitro-1-naphthoxide eparating on cooling was washed twice with 5% potash solution (50 c.c.), the filtrate and washings were warmed slightly and acidified with acetic acid, and the crude 4-nitronaphthol was filtered off and steam-distilled until the 2-nitro-1-naphthol present (0·3 g.) had been removed. The product was purified by boiling with animal charcoal and crystallised (yield, 9·5 g.; m. p. 165—166°). The otassium 2-nitro-1-naphthoxide, acidified in boiling aqueous solu-ion with acetic acid, gave the free nitronaphthol, which was filtered ff while hot (yield, 9 g.; m. p. 128—129°). The filtrate deposited trace of 4-nitro-1-naphthol.

A simple separation was not effected if sodium hydroxide was sed instead of potassium hydroxide in the hydrolysis.

Conversion of Nitrophenols and Nitronaphthols into Sulphates compare Ashworth, Burkhardt, and Lapworth, *loc. cit.*).—Chloro-ulphonic acid (1·4 mols.) was added to dimethylaniline (3·7 mols.) n carbon disulphide (500 c.c.), kept below 16°. To the mixture, nade mobile by heating to 35°, nitrophenol or nitronaphthol 1 mol.) was added all at once. After an hour's stirring at 35° the roduct was kept over-night and then poured into a well-stirred olution of caustic potash (4 mols.) in water (2 l. for *o*-nitrophenol, l. for *p*-nitrophenol, 2·5 l. for 1-nitro-2-naphthol, and 5 l. for -nitro-1-naphthol), kept below 30°.

In the case of *o*-nitrophenol the base was separated directly by

the addition of a little benzene; ice was then added and when the temperature had fallen to 5° hydrochloric acid was added until all the unchanged nitrophenol had just separated. The solution was filtered, at once made alkaline again with caustic potash, and heated to 50°, and the requisite amount of barium chloride solution was added to convert nearly all the residual potassium sulphate into chloride. On evaporation under reduced pressure the solution gave potassium *o*-nitrophenyl sulphate (80% of the theoretical yield) as a first fraction. If the bulk of the potassium sulphate was not converted into chloride before evaporation, it crystallised with the required product, which was then only obtained pure by a tedious extraction with hot 90% alcohol.

In the case of *p*-nitrophenol the extraction liquor had to be heated to 50° to dissolve the solid matter, and the base was then separated directly while hot by the addition of a little toluene. A short evaporation under reduced pressure completed the removal of the base. Some pure potassium *p*-nitrophenyl sulphate separated on cooling and the remainder was obtained by evaporation under reduced pressure, after the unchanged *p*-nitrophenol had been removed by ether extraction of the solution acidified below 5°. Yield, 80%.

The case of the 1-nitro-2-naphthol was the most difficult in the extraction. The large amount of solid which separated was removed and dissolved in the minimum amount of warm water and this solution and the original filtrate were treated in parallel. The base was separated with benzene, the solution cooled and acidified and the unchanged nitronaphthol (55%) separated. The solutions made alkaline with potash, were evaporated under reduced pressure until the required product crystallised (yield, 40%). A further crystallisation from water at 70° was sometimes necessary.

Potassium 4-nitro-1-naphthyl sulphate separated from the alkaline liquor contaminated only with dimethylaniline, which was removed by washing with methylated spirit. The filtrate was treated as usual and a further quantity isolated. One recrystallisation from hot water gave a pure product (yield, 85%).

Potassium o-*nitrophenyl sulphate* was recrystallised from 90% alcohol and then from water (Found: K, 15·3. $C_6H_4O_6NSK$ requires K, 15·2%). The solubility in water at 17° is 16%. It is very sparingly soluble in hot or cold alcohol, but readily in cold 70% alcohol or hot 90%.

Potassium p-*nitrophenyl sulphate* was recrystallised from water (Found: K, 15·1%). The solubility in water at 17° is 8%. It is very sparingly soluble in hot or cold alcohol or aqueous alcohol.

Potassium 1-nitro-2-naphthyl sulphate is sparingly soluble in cold

water and crystallises from hot water in long, pale yellow needles (Found: K, 11·95. $C_{10}H_{8}O_{6}NSK,H_{2}O$ requires K, 12·0%).

Potassium 4-nitro-1-naphthyl sulphate is sparingly soluble in cold water and crystallises from hot water in fine, pale yellow needles (Found: K, 12·7. $C_{10}H_{6}O_{6}NSK$ requires K, 12·7%).

All these compounds are rapidly hydrolysed by very dilute hydrochloric acid at about 70°, and slowly at 100° by 10% barium hydroxide solution or dilute acetic acid containing sodium acetate [contrast to potassium phenyl and naphthyl sulphates (Burkhardt and Lapworth, *loc. cit.*), and sodium acetyl sulphate, which is rapidly hydrolysed by cold water (von Peski, *Rec. trav. chim.*, 1921, **40**, 103)]. The hydrolysis with barium hydroxide or acetic acid is still incomplete after 6 hours. An even slower hydrolysis takes place with aqueous ammonia, which behaves as a weak alkali and shows no sign of replacing the sulphate group, attached to the benzene ring, by an amino-group.

Reduction of Nitrophenyl and Nitronaphthyl Sulphates.—A warm concentrated solution of potassium nitrophenyl or nitronaphthyl sulphate (0·1 mol.) was added in small portions during 1·5 hours to a suspension of precipitated calcium carbonate (1·5 mols.) or barium carbonate (1·2 mols.) in a solution of ferrous sulphate (0·9 mol.) in water (600 c.c.) kept at 70—75° and repeatedly shaken. Barium carbonate was only used for 1-nitro-2-naphthyl sulphate; in this case the reaction, after further addition of ferrous sulphate (0·2 mol.) and barium carbonate (0·25 mol.), was complete only after 4 hours. The liquid was filtered hot, the residue washed with hot water, and the filtrate treated with barium hydroxide (if calcium carbonate was used) to precipitate all the free sulphate ion; passage of carbon dioxide then precipitated all the barium and calcium. The filtered solution was made alkaline with caustic potash and evaporated almost to dryness under reduced pressure, and the product crystallised from 80% alcohol. Yields: potassium *o*- and *p*-aminophenyl sulphates and 1-amino-2-naphthyl sulphate, 90%; 4-amino-1-naphthyl sulphate, 66%.

From solutions of potassium *p*-aminophenyl sulphate and potassium 4-amino-1-naphthyl sulphate the free acids were precipitated by hydrochloric or acetic acid.

Preparation of benzylidene derivative. A mixture of potassium *p*-aminophenyl sulphate (3 g.) and benzaldehyde (6·5 c.c.) was warmed at 70° for 30 minutes, cooled, suspended in a little benzene, and filtered. After being washed with a little benzene, the solid product contained about 85% of the benzylidene derivative, the rest being unchanged material. It was recrystallised from 80% alcohol containing a trace of potash.

Acetylation of amino-groups. Potassium *o*- or *p*-aminophenyl sulphate (3 g.) was dropped into 5 c.c. of acetic anhydride with stirring and water-cooling. The solid product was recrystallised from 80% alcohol (20 c.c.) containing a trace of potash (yield, over 90%).

Acid hydrolysis of the acetyl derivative. A concentrated solution of potassium *p*-acetamidophenyl sulphate was acidified with dilute hydrochloric acid and boiled for 3·5 minutes. On cooling, neutralising, and evaporating it, a 50% yield of crude *p*-acetamidophenol was obtained which was purified (m. p. 166°) by two recrystallisations from aqueous alcohol. A large amount of hydrolysis of the acetyl group had also taken place.

Potassium o-*aminophenyl sulphate* (Found : K, 17·1. $C_6H_6O_4NSK$ requires K, 17·2%) is very soluble in water, but a saturated solution gives no precipitate of the internal salt with acids. Bromine water causes a faint violet coloration. No precipitate is formed on the addition of excess of bromine unless the solution has been acidified, in which case a bright yellow precipitate, soluble in ether, is produced. Ferric chloride gives no coloration.

The p-*aminophenyl sulphate* (Found : K, 15·9. $C_6H_6O_4NSK,H_2O$ requires K, 15·9%) is extremely soluble in water and crystallises from 80% alcohol in poorly defined tablets. Hydrochloric or acetic acid gives a crystalline precipitate of the hydrogen aminophenyl sulphate. Bromine produces a violet coloration in acid solution. This colour is discharged by excess of bromine and a yellow precipitate, readily soluble in ether, is formed which crystallises from aqueous alcohol in nearly colourless plates, m. p. 124°. Ferric chloride gives no coloration.

Hydrogen p-*aminophenyl sulphate* is sparingly soluble in all solvents. Small quantities can be crystallised from warm water, but it is best obtained pure by precipitation from solutions of the pure potassium salt. It is soluble in alkalis, alkali carbonates, ammonia, and excess of potassium acetate, although acetic acid gives a precipitate with solutions of the potassium salt (Found : equiv., with sodium hydroxide, 190. $C_6H_7O_4NS$ requires equiv., 189).

Potassium p-*benzylideneaminophenyl sulphate* (Found : K, 12·1. $C_{13}H_{10}O_4NSK,\frac{1}{2}H_2O$ requires K, 12·1%) is sparingly soluble in cold water, almost insoluble in hot or cold alcohol, but fairly readily soluble in hot aqueous alcohol. On warming with dilute acid to about 50°, benzaldehyde is liberated, and a small amount of hydrogen *p*-aminophenyl sulphate separates on cooling; at the same time the sulphate group is partly removed.

Potassium 1-*amino*-2-*naphthyl sulphate* (Found : K, 13·6. $C_{10}H_8O_4NSK,\frac{1}{2}H_2O$ requires K, 13·7%) crystallises from hot water

in slightly pink plates. The solubility in water at 17° is 1·1%. Acids do not precipitate the internal salt from a saturated solution (compare *o*-aminophenyl sulphate). Bromine water gives a dirty green precipitate which changes to yellow with excess of bromine and becomes soluble in ether, from which it crystallises in yellow needles. This precipitate is also slightly soluble in alkali, giving a dark green solution. Ferric chloride gives first an opalescence and then a blue precipitate which changes to brown.

Potassium 4-amino-1-naphthyl sulphate forms hydrated, apparently efflorescent needles from aqueous alcohol. From concentrated solutions hydrochloric or acetic acid precipitates microscopic needles of *hydrogen 4-amino-1-naphthyl sulphate* (Found: equiv., 241. $C_{10}H_9O_4NS$ requires equiv., 239). This crystallises from much hot water in long needles.

All these potassium aminoaryl sulphates can be boiled in dilute mineral acid solution for a few seconds before hydrolysis is detectable. They are thus rather more difficult to hydrolyse than potassium phenyl sulphate itself. Excess of bromine completely removes the sulphate group.

Diazotisation of Aminophenyl and Aminonaphthyl Sulphates.—Hydrogen *p*-aminophenyl sulphate (4·15 g.), suspended in water (40 c.c.), was cooled to 5°, concentrated hydrochloric acid (3 c.c.) added, and *N*-potassium nitrite (1 mol.) run in. The solid product showed all the properties of the diazo-derivative. The method for the naphthyl sulphate was similar.

Coupling with phenols and naphthols. The whole of the suspension obtained in the diazotisation above was poured slowly into a cold solution of resorcinol (2·75 g.) in water (40 c.c.) containing an excess of potassium carbonate. The reddish-orange solution obtained was treated with acetic acid after 1·5 hours and *potassium dihydroxybenzeneazophenyl sulphate* separated (yield, 88%). This crystallised from hot water in orange plates, sparingly soluble in cold water, readily in hot water, alkalis, or alkaline carbonates, and insoluble in alcohol and other organic solvents (Found: K, 10·5. $C_{12}H_9O_6N_2SK,1\frac{1}{2}H_2O$ requires K, 10·4%). An aqueous solution boiled with dilute hydrochloric acid for 15 minutes gave dihydroxybenzeneazophenol as a powder (yield, over 90%), which crystallised in feathery needles from alcohol.

A diazo-solution, prepared as above and run into a solution (50 c.c.) of β-naphthol (3·2 g.) and potassium hydroxide (2·55 g.), gave, after an hour's stirring, a dark red azo-dye containing the sulphate group (yield, 85%); a further quantity was obtained by salting out with potassium chloride.

Potassium 2-hydroxynaphthaleneazophenyl sulphate, crystallised

from 20% aqueous alcohol, is sparingly soluble in cold water and alcohol and moderately easily soluble in hot water (Found: K, 10·1. $C_{16}H_{11}O_5N_2SK,\frac{1}{2}H_2O$ requires K, 10·0%). It forms red flocculent precipitates in neutral solution with barium and calcium chlorides, bright orange-red needles with mercurous nitrate, and a brown flocculent precipitate with magnesium sulphate. No insoluble salts are formed on adding silver, lead, copper, ferrous, ferric, mercuric and aluminium salts. The sulphate group is rapidly and quantitatively removed on boiling with dilute mineral acid, *p*-hydroxybenzeneazo-β-naphthol (dark purple needles, m. p. 193·5°, from aqueous alcohol; Niementowski, *Chem. Zentr.*, 1902, **73**, 938, gives 194°) being formed.

Potassium 4-2′-hydroxynaphthaleneazo-1-naphthyl sulphate is a red solid, fairly easily soluble in warm water. The free acid is precipitated almost completely on addition of mineral acid to a cold solution of the potassium salt, and if the mixture is then boiled the sulphate group is removed, a dark red precipitate of 4-hydroxy-naphthaleneazo-β-naphthol, m. p. 236°, being formed (Niementowski, *loc. cit.*, gives 228—229°).

Dyeings with these Sulphato-azo Dyes (V and VI).—Wool patterns (5 g. each) were dyed in the usual manner in dye-baths (total volume, 400 c.c.) containing 0·10 g. of dye, 0·15 g. of sulphuric acid, and 0·50 g. of sodium sulphate. Half of each pattern was then replaced in half of the exhausted dye-bath, restored to its proper volume (200 c.c.) after the addition of sufficient sulphuric acid (40 c.c. of 5% acid) to form a 1% solution. After an hour's boiling, the shades had changed materially, (V) from a bright orange-scarlet to a dull brownish-orange and (VI) from deep red to a dull greyish-violet.

If solutions were made up similar to the above dye-baths but with the minimum of water and allowed to concentrate on the water-bath, complete hydrolysis and precipitation of the dyes were effected in the course of an hour or so. The hydrolysed dye from (V) was brought into partial solution by the addition of alcohol and water and a dyeing performed in this dye-bath; a dull brownish-orange shade resulted similar to that obtained by dyeing with (V) and subsequent hydrolysis with 1% acid: the latter shade, however, was necessarily slightly duller owing to the relatively drastic treatment involved in the hydrolysis on the fibre.

Action of Nitrous Acid on o-*Aminophenyl and* o-*Aminonaphthyl Sulphates.*—To potassium *o*-aminophenyl sulphate (1·5 g.) in water (20 c.c.) at 0°, concentrated hydrochloric acid (2 c.c.) was added, followed by the requisite amount of *N*-potassium nitrite. The product (which gave a precipitate in acid solution with barium

chloride) was run into β-naphthol (1 g.) in water (15 c.c.) containing caustic potash (1·2 g.), and after 3 hour's stirring excess of acetic acid was added. The precipitate was washed with water, dried, and extracted with ether to remove naphthol. It was insoluble in water and organic solvents and melted at 191°. Niementowski (*loc. cit.*) gives for *o*-hydroxybenzeneazo-β-naphthol, m. p. 193°.

The action of nitrous acid on potassium 1-amino-2-naphthyl sulphate and on the azo-derivative produced by coupling diazotised sulphanilic acid with 1-amino-2-naphthyl sulphate was examined, but more water was used to get as much of the amine into solution as possible. The resulting solutions gave precipitates with barium chloride, but did not couple with any alkaline phenoxide except resorcinol, with which they gave blue and dark green colours respectively. The precipitate obtained from 1-amino-2-naphthol hydrochloride and nitrous acid did not couple with resorcinol.

Naphthalene 1 : 2-diazo-oxide was separated in 96% yield from the aqueous solution, by four extractions with ether, as a yellow solid, m. p. 94—95° after recrystallisation from light petroleum (b. p. 60—80°). Bamberger (*Ber.*, 1894, **27**, 679) gives m. p. 95°.

Potassium 4 : 4′-diaminodiphenylene 3 : 3′-disulphate (I; see p. 151) was tetrazotised with excess of acid and excess of sodium acetate was subsequently added. The tetrazo-compound, which soon separated as orange needles, contained no sulphate group and was apparently identical with the bisdiazo-oxide obtained from 3 : 3′-dihydroxybenzidine (p. 151).

Alkaline Reduction of Potassium o-*Nitrophenyl Sulphate.—Reduction with zinc dust.* Caustic potash (0·27 g.) in water (50 c.c.) was added during 5 hours to a suspension of zinc dust (20 g.; 60% Zn) in a solution of potassium *o*-nitrophenyl sulphate (10 g.) in water (100 c.c.) with mechanical stirring at 60°; then, as reduction was incomplete, a few drops of potassium hydroxide solution were added from time to time, the temperature being raised to 70°, until no more nitro-compound remained (40 hours altogether). The solution was filtered, the residue was washed well with hot water, and the united filtrates were divided into two equal portions A and B.

Portion A was evaporated nearly to dryness under reduced pressure and the solid obtained was dissolved in 85% alcohol at 70°. On cooling, a mixture of the hydrazo-compound (colourless needles) and the azo-compound (yellow crystals) separated (0·8 g.). The filtrate, treated with ether, deposited a mixture containing more of the yellow compound (0·9 g.). Recrystallisations from 80% alcohol separated the two compounds (yield, 36% of the theoretical yield from 5 g. of nitrophenyl sulphate).

Portion B was treated with a few drops of hydrochloric acid in

the cold. The benzidine derivative was rapidly precipitated (0·76 g.; 19% from 5 g. of nitrophenyl sulphate, *i.e.*, 19% of the nitrophenyl sulphate is converted into hydrazo-compound and 17% into azo-compound).

Such modifications as the use of higher concentrations of nitro-compound, more alkali, purer zinc dust, higher temperature, and aqueous alcohol as the solvent gave smaller yields.

Reduction with sodium amalgam. 2% Sodium amalgam (130 g.) was added to a vigorously stirred solution of potassium *o*-nitrophenyl sulphate (2·69 g.) in water (50 c.c.) in the course of 3 hours. After standing over-night, the white solid was separated, washed with a little water and dissolved in warm water, and the solution was treated with hydrochloric acid, cooled rapidly, and filtered. The mother-liquor from the reduction was treated with zinc dust at 50—60° until the red colour had vanished; hydrochloric acid was then added to the filtered solution. Potassium 4 : 4′-diaminodiphenylene 3 : 3′-disulphate separated in both cases (0·69 g. and 0·46 g., respectively; yield, 52%).

Potassium azobenzene 2 : 2′-disulphate, $(KO{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}N{:})_2$, crystallises from hot water in orange hexagonal plates insoluble in organic solvents (Found: K, 16·9. $C_{12}H_8O_8N_2S_2K_2,\frac{1}{2}H_2O$ requires K, 17·0%). It is rapidly hydrolysed by hydrochloric acid at 70° (compare nitrophenyl sulphate), giving *oo*′-dihydroxyazobenzene, which crystallises from aqueous alcohol in yellow needles, m. p. 171° (Weselsky and Benedikt, *Ber.*, 1878, **11**, 398; *Annalen*, 1879, **196**, 344, give 171°). The orange-red solution in aqueous sodium hydroxide is rapidly decolorised by warming with zinc dust and then gives a white precipitate of the benzidine derivative when treated with hydrochloric acid.

Potassium hydrazobenzene 2 : 2′-disulphate crystallises from hot water in colourless feathery needles stable in the air. A cold neutral solution also resists oxidation, but the azo-compound is formed when air is passed through a warm alkaline solution and rapidly by warm ferric chloride or nitrous acid. The solubility in water is 3·2% at 19° and 5·4% at 32°. A saturated solution of the hydrazo-compound at 20°, when treated with concentrated hydrochloric acid (0·1 vol.), deposits a 95% yield of *4 : 4′-diaminodiphenylene dihydrogen* 3 : 3′-*disulphate* in a few minutes. This crystallises in colourless needles from a large bulk of water. It is insoluble in cold water, hot or cold alcohol and ether, but readily soluble in alkalis, ammonia, sodium carbonate and potassium acetate. It is rather more stable to acid hydrolysis than the aminophenyl sulphates [Found: equiv., 210. $C_{12}H_{10}N_2(SO_4H)_2,2\frac{1}{2}H_2O$ requires equiv., 211].

Potassium 4 : 4′*-diaminodiphenylene* 3 : 3′*-disulphate* (I) is prepared by the addition of a concentrated potassium hydroxide solution to a warm aqueous suspension of the free acid. It separates in elongated plates, usually slightly brown in colour (Found : K, 16·5. $C_{12}H_{10}O_8N_2S_2K_2,H_2O$ requires K, 16·6%). The free acid is precipitated from solutions of this salt by mineral acids but not by acetic acid (compare *p*-aminophenyl sulphate).

Characteristic colour reactions similar to those given by benzidine are obtained with bromine and ferric chloride. The cautious addition of very dilute bromine water causes the following series of colour changes : green, blue, olive-green, brown, red ; the last colour fades on standing and a test with barium chloride then shows that elimination of the sulphate group has taken place. An intense blue coloration or a dark blue precipitate is obtained with ferric chloride.

Hydrolysis to 3 : 3′*-dihydroxybenzidine.* A suspension of 3·33 g. of the sulphate in 150 c.c. of boiling water was boiled with concentrated hydrochloric acid (20 c.c.) for 2½ hours and the solution was then cooled, filtered, and treated with an excess of sodium acetate solution ; the light brown solid precipitated was washed with water and alcohol (yield, almost quantitative).

Demethylation of dianisidine. Powdered dianisdine (10 g.) and hydriodic acid (100 c.c., b. p. 127°) were heated in a bath at 138° ; after 24 hours the temperature was raised and the unused hydriodic acid distilled off. A solution of the residue in hot water was filtered, sodium bisulphite added to remove iodine, and the base precipitated with sodium acetate solution. The product was washed and boiled with alcohol to remove dianisidine (yield, 90%).

The dihydroxybenzidine obtained by these two methods is a white powder, slowly darkening on exposure to air, very soluble in alkalis and in hot dilute mineral acids, very sparingly soluble in hot water and organic solvents, and soluble in, but not crystallisable from, hot 80—90% acetic acid. A solution of the hydrochloride in water, when treated with sodium nitrite solution, deposits orange needles which explode violently when heated and show a low reactivity to most phenols. It combines slowly with R-salt and Schäffer's acid in alkaline solution to form purple-blue substantive dyes, rather redder than those from dianisidine. A blue insoluble dye is slowly formed with sodium β-naphthoxide and a fine crimson colour is at once formed with alkaline resorcinol. No combination took place with Naphthol AS.

Acetylation of dihydroxybenzidine. Dihydroxybenzidine was dissolved by boiling with glacial acetic acid (50 c.c.) with subsequent addition of water (12 c.c.). The solution was filtered and acetic

anhydride (50 c.c.) added at about 50°. The almost colourless solid was filtered off after 36 hours and washed with acetic acid (yield, 90%). *Diacetyldihydroxybenzidine* is insoluble in most organic solvents. After crystallising from benzyl alcohol and drying at 150°, it melts at 292° (decomp.) (Found: N, 9·2. $C_{16}H_{16}O_4N_2$ requires N, 9·3%). It is insoluble in acids, but readily soluble in alkalis. An attempt to methylate it to diacetyldianisidine did not give any product insoluble in alkali.

Dehydration. The diacetyl compound (0·75 g.) was heated at 300—320° for ¾ hour and the *dianhydro*-derivative (IV) extracted from the dark mass with boiling alcohol. The extract was filtered and diluted at its boiling point with water, a little animal charcoal added, and the filtered solution allowed to crystallise (yield, 45%). The anhydro-compound is very soluble in benzene, chloroform, acetic acid and hot alcohol and crystallises from the last solvent in ill-defined plates, m. p. 164—165° (Found: N, 10·5. $C_{16}H_{12}O_2N_2$ requires N, 10·6%). It is insoluble in hot alkalis but dissolves in concentrated hydrochloric acid. If this solution is diluted somewhat and heated, dihydroxybenzidine remains in the solution as the hydrochloride. A white precipitate which was noticed in some experiments was dissolved by caustic soda and was probably the diacetyl derivative.

The dihydroxybenzidine obtained from the sulphate was also converted into the diacetyl compound and its dianhydro-derivative and these were shown to be identical with those described above.

The authors gratefully acknowledge their indebtedness to Professor Lapworth for his interest in this investigation and to the Department of Scientific and Industrial Research for maintenance grants which enabled them to undertake it.

THE UNIVERSITY, MANCHESTER. [*Received, October 10th,* 1928.]

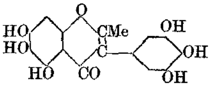
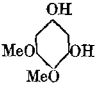
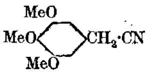
XXII.—*Synthetical Experiments in the* iso*Flavone Group. Part IV. A Synthesis of 2-Methylirigenol.*

By WILSON BAKER and ROBERT ROBINSON.

IRIGENOL, obtained by the demethylation of irigenin (de Laire and Tiemann, *Ber.*, 1893, **26**, 2010), has recently been proved to be 5 : 6 : 7 : 3′ : 4′ : 5′-hexahydroxy*iso*flavone (Baker, *J.*, 1928, 1022). The synthesis of *2-methylirigenol* (I) is now described and a comparison of this substance with irigenol itself fully substantiates the correctness of the previous work. This paper is, therefore, Part IV

of the series *Synthetical Experiments in the* isoFlavone *Group* and also Part II of *The Constitution of Irigenin and Iridin*.

The synthesis was carried out by methods which have been used to prepare other 2-substituted *iso*flavones (Baker and Robinson, Part I, J., 1925, **127**, 1981; Part II, 1926, 2713; Part III, 1928, 3115), the starting materials being 4 : 5-dimethoxyresorcinol (II) and 3 : 4 : 5-*trimethoxyphenylacetonitrile* (III).

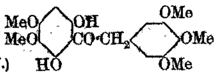
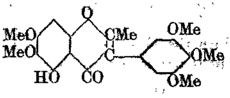




(I.) (II.) (III.)

4 : 5-Dimethoxyresorcinol (II) has recently been obtained by hydrolysis of irigenin 5 : 3'- and 7 : 3'-dimethyl ethers (Baker, *loc. cit.*), and has been synthesised by Chapman, Perkin, and Robinson (J., 1927, 3015) from 4 : 6-dinitroguaiacol through 3 : 5(4 : 6)-dinitroveratrole and 3 : 5(4 : 6)-diaminoveratrole. The tedious processes involved in the preparation of (II) have been somewhat simplified by the observation that 4 : 6-dinitroguaiacol can be obtained in excellent yield by the direct nitration of guaiacol in ethereal solution with nitrous fumes. The nitrile (III) was prepared from 3 : 4 : 5-trimethoxybenzaldehyde, which was itself obtained by the reduction of the corresponding acid chloride in boiling xylene solution with hydrogen in the presence of palladinised barium sulphate, an application of Rosenmund's method (*Ber.*, 1918, **51**, 585, 591). Condensation of the aldehyde with hippuric acid, followed by alkaline hydrolysis of the azlactone, gave 3 : 4 : 5-trimethoxyphenylpyruvic acid, the oxime of which when heated with acetic anhydride gave (III).

Condensation of (II) and (III) under the conditions of the Hoesch synthesis gave as the only product 2 : 6-*dihydroxy*-3 : 4-*dimethoxyphenyl* 3 : 4 : 5-*trimethoxybenzyl ketone* (IV). The constitution

(IV.)

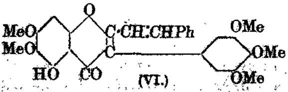
(V.)

assigned to this ketone follows from the fact that the chromone produced by boiling it with a mixture of acetic anhydride and sodium acetate and then hydrolysing the acetoxy-group has the properties of a 5- and not a 7-hydroxy-derivative. Its phenolic function is very weak and its behaviour with ferric chloride leaves no doubt that the free hydroxyl group occupies position 5. This

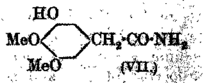
reactivity of 4 : 5-dimethoxyresorcinol in position 2 has already been observed in the preparation of 2 : 6-dihydroxy-ω : 3 : 4-trimethoxyacetophenone by its condensation with methoxyacetonitrile (Baker, Nodzu, and Robinson, this vol., p. 74). The direction of ring closure was established by methylating the free hydroxyl group by vigorous treatment with methyl sulphate and decomposing the product with alkali; antiarol (3 : 4 : 5-trimethoxyphenol) and 3 : 4 : 5-trimethoxyphenylacetic acid were then obtained. The methylated chromone was therefore 5 : 6 : 7 : 3′ : 4′ : 5′-*hexamethoxy-2-methylisoflavone* (*2-methylirigenin trimethyl ether*), and the deacetylated product of the ring closure was 5-*hydroxy-6 : 7 : 3′ : 4′ : 5′-pentamethoxy-2-methylisoflavone* (*2-methylirigenin 7 : 3′-dimethyl ether*) (V). It appears to be a general rule that when a derivative of 1 : 2 : 3 : 5-tetrahydroxybenzene undergoes ring closure, it is the hydroxyl group in position 5 which is concerned. For instance, Bargellini (*Gazzetta*, 1919, **49**, 47), by heating 2 : 3 : 4 : 6-tetramethoxyphenyl phenacyl ketone with hydriodic acid, obtained 5 : 6 : 7-trihydroxyflavone or, by heating for a short time only, 5 : 6 : 7-trimethoxyflavone, and in a similar manner (*ibid.*, 1915, **45**, 69) 2 : 3 : 4 : 6-tetramethoxyphenyl *p*-methoxyphenacyl ketone gave only 5 : 6 : 7 : 4′-tetrahydroxyflavone (scutellarein). Again, Chapman, Perkin, and Robinson (*loc. cit.*) showed that iretol yielded pyrylium salts having hydroxyl groups in positions 5, 6, and 7, and finally 2 : 6-dihydroxy-ω : 3 : 4-trimethoxyacetophenone, when heated with veratric anhydride and sodium veratrate, gave quercetagetin pentamethyl ether (Baker, Nodzu, and Robinson, *loc. cit.*).

Demethylation of (V) gave 5 : 6 : 7 : 3′ : 4′ : 5′-*hexahydroxy-2-methylisoflavone* (*2-methylirigenol*) (I). In its appearance, reactions with alkali, ferric chloride, etc., it is indistinguishable from irigenol and, as a dye, the colours produced on wool mordanted with aluminium, tin, chromium, and iron are identical with those given by irigenol. (The dyeing properties of 2-methylgenistein—not previously recorded—are identical with those of genistein itself.)

With the object of synthesising irigenin trimethyl ether by the methods previously used (Parts I, II, and III), the ketone (IV) was



(VI.)



(VII.)

heated with a mixture of cinnamic anhydride and sodium cinnamate, giving 5-*hydroxy-6 : 7 : 3′ : 4′ : 5′-pentamethoxy-2-styrylisoflavone* (VI).

The methyl ether of this compound could not be successfully oxidised in pyridine solution with potassium permanganate to a substituted *iso*flavone-2-carboxylic acid, but the labour involved in its preparation prevented the experiment from being carried out on as large a scale as was desirable.

Iridamide (3-*hydroxy*-4 : 5-*dimethoxyphenylacetamide*) (VII) was prepared by the action of aqueous ammonia upon methyl iridate. Attempts to bring about direct dehydration to the nitrile were unsuccessful.

The Reactivity of Some Phenolic Ethers.

The persistent reactivity of 4 : 5-dimethoxyresorcinol in position 2 has led to the investigation of the reactive centres of other phenolic ethers under parallel conditions.

Resorcinol monomethyl ether was found by Gattermann (*Annalen*, 1907, **357**, 346) to give only 4-hydroxy-2-methoxybenzaldehyde, and Hoesch (*Ber.*, 1915, **48**, 1122) found that by the action of acetonitrile it gave about equal quantities of the two isomeric ketones pæonol and *iso*pæonol. It has now been found that the Hoesch synthesis with phenylacetonitrile gives approximately 3 parts of 2-hydroxy-4-methoxyphenyl benzyl ketone to 1 part of 4-*hydroxy*-2-*methoxyphenyl benzyl ketone*, the orientation of the first being established by ring closure with sodium acetate and acetic anhydride to 7-methoxy-2-methyl*iso*flavone. It has usually been found that this closure could not be effected with derivatives of pæonol (Crabtree and Robinson, J., 1918, **113**, 864; Baker and Robinson, J., 1925, **127**, 1430), but it appears that the reaction takes place if a large excess of the reagents is used and sufficient time is allowed (compare Nagai, *Ber.*, 1892, **25**, 1284; Kostanecki and Rózycki, *Ber.*, 1901, **34**, 102).

Phloroglucinol monomethyl ether yields an aldehyde by Gattermann's reaction (Herzig and Wenzel, *Monatsh.*, 1903, **24**, 857) shown by Pratt and Robinson (J., 1924, **125**, 188) to be 2 : 4-dihydroxy-6-methoxybenzaldehyde. The Hoesch reaction with *n*-butyronitrile (Karrer, *Helv. Chim. Acta*, 1919, **2**, 466) gives a mixture of 2 : 4-dihydroxy-6-methoxyphenyl *n*-propyl ketone and 2 : 6-dihydroxy-4-methoxyphenyl *n*-propyl ketone, and benzonitrile (*idem*, *ibid.*, p. 486) gives only 2 : 4-dihydroxy-6-methoxybenzophenone (*iso*cotoin).

Orcinol monomethyl ether was found by Gattermann (*loc. cit.*) to give only 4-hydroxy-2-methoxy-6-methylbenzaldehyde, this orientation being confirmed by Hirst (J., 1927, 2490), and Hoesch (*loc. cit.*) prepared from it by the action of acetonitrile a mixture of the 2-methyl ether of orcacetophenone and a slightly smaller

amount of the corresponding 4-methyl ether. The Hoesch reaction with phenylacetonitrile (this paper) gives chiefly 4-*hydroxy-2-methoxy-6-methylphenyl benzyl ketone* and about one-sixth the amount of 2-*hydroxy-4-methoxy-6-methylphenyl benzyl ketone*. The orientation of the last substance was established by conversion into 7-*methoxy-2 : 5-dimethylisoflavone*.

EXPERIMENTAL.

4 : 6-*Dinitroguaiacol*.—A mixture of concentrated hydrochloric acid (425 c.c.) and water (425 c.c.) was gradually added during several hours to a solution of sodium nitrite (250 g.) in water (1 l.) underlying one of guaiacol (50 g.) in ether (750 c.c.) (compare dinitration of *iso*creosol; Graesser-Thomas, Gulland, and Robinson, J., 1926, 1973). After 12 hours, the ether was removed in a current of air, leaving dinitroguaiacol, m. p. 119—121·5° (47 g.).

3 : 5(4 : 6)-*Dinitroveratrole*.—Methyl sulphate (150 g., redistilled) was added to a constantly stirred mixture of 4 : 6-dinitroguaiacol (50 g.), potassium carbonate (75 g.), and xylene (25 c.c.) heated for 2 hours at 130°. Water (500 c.c.) was added, the xylene distilled off, and the hot solution rendered alkaline by sodium hydroxide and cooled while being shaken (yield, 55 g.; m. p. 99—100°).

3 : 5(4 : 6)-*Diaminoveratrole and* 4 : 5-*Dimethoxyresorcinol* (II) (see Chapman, Perkin, and Robinson, *loc. cit.*).—3 : 5-*Diaminoveratrole* crystallises from alcohol in colourless, approximately octahedral crystals, m. p. 106° (Found: C, 57·1; H, 7·3; N, 16·8. $C_8H_{12}O_2N_2$ requires C, 57·1; H, 7·2; N, 16·7%). It is readily soluble in water; the solution darkens on keeping and gives a reddish-brown coloration with nitrous acid. The dimethoxyresorcinol is best obtained, after the hydrolysis, by extraction with chloroform and is then crystallised directly from a little water (charcoal), large prisms of the monohydrate, m. p. 74°, separating. By heating to 100° it melts and then solidifies to the anhydrous substance, m. p. 115°. Yield from 30 g. of dinitroveratrole, about 5 g. The unhydrolysed diamine may be recovered by concentration and hydrolysed as before.

3 : 4 : 5-*Trimethoxybenzaldehyde*.—This substance was first prepared by Stephen's method (J., 1925, **127**, 1874), but the process is tedious and not suitable for the preparation of the aldehyde in quantity, the yields being only about 10—20% from the nitrile.

3 : 4 : 5-Trimethoxybenzoyl chloride (25 g.) in dry xylene (100 c.c.) was reduced at the boiling point in the presence of palladinised barium sulphate (5 g.; *Ber.*, 1919, **52**, 409) by a slow stream of pure hydrogen for 6 hours (see Rosenmund, *loc. cit.*). Evolution of hydrogen chloride ceased in about 5 hours. The filtered liquor

was shaken with saturated sodium bisulphite solution (45 c.c.) and the solid bisulphite compound was filtered off, washed with ether, and decomposed with hydrochloric acid, yielding the pure aldehyde, m. p. 74—75° (10—11 g.).

3 : 4 : 5-*Trimethoxyphenylpyruvic Acid.*—The condensation of the foregoing aldehyde with hippuric acid, the hydrolysis to the substituted pyruvic acid, and the preparation of its oxime have been described by Mauthner (*Ber.*, 1908, **41**, 3662), who, however, worked with very small quantities. Since, moreover, difficulty was experienced with the initial condensation and the subsequent steps proved to be unnecessarily tedious, the simpler methods used in this investigation are recorded.

3 : 4 : 5-Trimethoxybenzaldehyde (15 g.), hippuric acid (22·5 g.), and anhydrous sodium acetate (7·5 g.) were finely ground and heated in a boiling water-bath with acetic anhydride (40 c.c.) for 6 minutes while being constantly stirred; the bright yellow, crystalline precipitate at first produced just dissolved. Alcohol (10 c.c.) was added to the cooled mixture and the azlactone was collected and washed with alcohol and with hot water (average yield, 17 g.). The azlactone (30 g.) was boiled with a solution of sodium hydroxide (15 g.) in water (90 c.c.) for 1 hour, water (100 c.c.) was added, the solution saturated with sulphur dioxide (compare Haworth, Perkin, and Rankine, J., 1924, **125**, 1693), and after a few hours the benzoic acid was filtered off. The filtrate was heated on the water-bath with excess of hydrochloric acid for 1 hour; 3 : 4 : 5-trimethoxyphenylpyruvic acid (16—17 g.) was then deposited. The quinoxaline derivative (Mauthner, *loc. cit.*), prepared by condensation with *o*-phenylenediamine, crystallised from alcohol in tiny needles, m. p. 196—197°, containing ½EtOH (Found in material dried at 100°: N, 8·0. Found in material dried at 130°: N, 8·5. Calc. for $C_{18}H_{18}O_4N_2,\frac{1}{2}EtOH$: N, 8·0%. Calc. for $C_{18}H_{18}O_4N_2$: N, 8·6%).

3 : 4 : 5-*Trimethoxyphenylacetonitrile* (III).—3 : 4 : 5-Trimethoxyphenylpyruvic acid (10 g.) and hydroxylamine hydrochloride (8 g.) dissolved in aqueous sodium hydroxide (100 c.c.; 8%) were warmed at 50° for a few minutes. After 12 hours, addition of hydrochloric acid threw down the oxime as an oil which rapidly crystallised (10 g.). The dry oxime (10 g.) was heated with acetic anhydride (5 c.c.) on the steam-bath and when the vigorous reaction had abated (2—3 minutes) water (50 c.c.) was added and the mixture shaken. The product rapidly crystallised and was collected and washed with dilute sodium bicarbonate solution. 3 : 4 : 5-*Trimethoxyphenylacetonitrile* crystallises from benzene–ligroin or from carbon tetrachloride in irregular fern-like crystals, m. p. 77° (Found:

C, 63·6; H, 6·1; N, 6·8. $C_{11}H_{13}O_3N$ requires C, 63·7; H, 6·3; N, 6·8%). The corresponding 3 : 4 : *5-trimethoxyphenylacetamide* was prepared by dissolving the nitrile (5 g.) in 95% sulphuric acid (25 c.c.) and after 24 hours pouring the solution on crushed ice and extracting the amide with chloroform. The extracts were shaken with a little saturated sodium bicarbonate solution and yielded a solid residue which crystallised from benzene in prismatic needles, m. p. 121° (Found: N, 6·2. $C_{11}H_{15}O_4N$ requires N, 6·2%).

2 : *6-Dihydroxy-3* : *4-dimethoxyphenyl* 3 : 4 : *5-Trimethoxybenzyl Ketone* (IV).—A solution of 3 : 4 : 5-trimethoxyphenylacetonitrile (2·1 g.) and anhydrous 4 : 5-dimethoxyresorcinol (1·8 g.) in dry ether (60 c.c.) was saturated with hydrogen chloride at 0° in presence of anhydrous zinc chloride (0·5 g.). After 12 hours, the ketimine was completely precipitated by the addition of dry ether (100 c.c.), washed with ether, and hydrolysed by boiling for ½ hour with dilute hydrochloric acid (50 c.c.). The ketone (2 g.) crystallised from methyl alcohol (charcoal) in tiny colourless prisms, m. p. 162° (Found: C, 60·1; H, 6·0. $C_{19}H_{22}O_8$ requires C, 60·3; H, 5·9%). No isomeric ketone could be detected in the mother-liquors. 2 : 6-*Dihydroxy-3* : *4-dimethoxyphenyl* 3 : 4 : *5-trimethoxybenzyl ketone* gives pale yellow solutions in dilute alkalis and in concentrated sulphuric acid, and its alcoholic solution develops a dull greenish-violet colour with a trace of ferric chloride, changing to dull greyish-olive with excess.

5-*Hydroxy*-6 : 7 : 3′ : 4′ : 5′-*pentamethoxy-2-methyl*iso*flavone* (2-*Methylirigenin* 7 : 3′-*Dimethyl Ether*) (V).—The ketone (IV) (1·5 g.), anhydrous sodium acetate (1·5 g.), and acetic anhydride (10 c.c.) were heated at 180° for 6 hours. The homogeneous *acetyl* derivative, isolated by shaking the product with dilute hydrochloric acid, crystallised from alcohol in small colourless prisms, m. p. 232—233° (Found: C, 62·0; H, 5·6. $C_{23}H_{24}O_9$ requires C, 62·1; H, 5·5%). The parent substance was obtained by heating the acetyl derivative in alcohol for a few minutes with a little concentrated potassium hydroxide solution. Addition of water threw down tiny crystals which subsequently separated from alcohol in very pale yellow, silky needles, m. p. 179—180° (Found: C, 62·4; H, 5·6. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%). This substance (V) is quite insoluble in aqueous alkalis, but dissolves readily in alcoholic potassium hydroxide to a bright yellow solution. Its alcoholic solution gives an intense, dull violet colour with a trace of ferric chloride, changing to deep olive-green with excess. In these ways its behaviour resembles that of the corresponding irigenin 7 : 3′-dimethyl ether.

5 : 6 : 7 : 3′ : 4′ : 5′-*Hexamethoxy-2-methylisoflavone* (2-*Methyliri-*

genin Trimethyl Ether).—The compound (V) was treated in boiling methyl-alcoholic solution with a large excess of methyl sulphate and methyl-alcoholic potassium hydroxide. Addition of water caused the precipitation of crystals, which were suspended in a little methyl alcohol and, after addition of a few drops of alkali to dissolve a trace of unmethylated substance, were collected and crystallised from methyl alcohol, giving small, colourless, lustrous prisms, m. p. 166° (Found: C, 63·3; H, 5·8. $C_{22}H_{24}O_8$ requires C, 63·4; H, 5·8%). Decomposition with concentrated alkali at 180° and isolation of the products as described in the case of irigenin trimethyl ether (Baker, *loc. cit.*) gave antiarol, m. p. 147°, and 3 : 4 : 5-trimethoxyphenylacetic acid, m. p. 120°.

5 : 6 : 7 : 3′ : 4′ : 5′-*Hexahydroxy-2-methyl*iso*flavone* (2-*Methylirigenol*) (I).—Demethylation of (V) was effected by heating with 10 times its weight of hydriodic acid (*d* 1·7) at 130° for 1 hour. The product, isolated by the addition of water, crystallised from 50% acetic acid in tiny, glistening, yellow prisms, m. p. 325° (decomp., rapid heating) (Found: C, 53·3; H, 4·3; H_2O, 7·2. $C_{16}H_{12}O_8,1\frac{1}{2}H_2O$ requires C, 53·5; H, 4·2; H_2O, 7·5%). 2-*Methylirigenol* in its appearance and in its behaviour with alkali, ferric chloride, and sodium amalgam in alcoholic solution is indistinguishable from irigenol, but is rather more soluble in the usual organic solvents. Methylation with methyl sulphate in an atmosphere of hydrogen gave its hexamethyl ether, m. p. 166°, identical with the methyl ether of 5-hydroxy-6 : 7 : 3′ : 4′ : 5′-pentamethoxy-2-methyl*iso*flavone.

5-*Hydroxy*-6 : 7 : 3′ : 4′ : 5′-*pentamethoxy-2-styryl*iso*flavone* (VI).—The cinnamoylation of the ketone (IV) was effected as described in Part II (*loc. cit.*) for the preparation of 5 : 7-dihydroxy-4′-methoxy-2-styryl*iso*flavone. After hydrolysis of the product with alcoholic potassium hydroxide and dilution, the substance was precipitated with carbon dioxide and successively crystallised from alcohol, acetic acid, and ethyl acetate, being obtained in tiny bright yellow needles, m. p. 270° (Found: C, 68·3; H, 5·6. $C_{28}H_{26}O_8$ requires C, 68·5; H, 5·4%). It is insoluble in aqueous alkalis and very sparingly soluble in alcohol; the solution, however, develops a brownish-green coloration with ferric chloride. The *methyl ether* was obtained by shaking an acetone solution with methyl sulphate and aqueous potassium hydroxide (compare methylation of 5-hydroxy-7 : 4′-dimethoxy-2-styryl*iso*flavone; Baker and Robinson, Part III, *loc. cit.*). The pale yellow product was suspended in methyl alcohol containing a little potassium hydroxide, collected, and crystallised repeatedly from methyl alcohol, being ultimately obtained in very pale yellow, hair-like needles, m. p. 214—215°,

It exhibits no colour with ferric chloride, and gives no alkali salt in acetone or other solvents.

Iridamide (VII).—The alkaline hydrolysis of irigenin (20 g.) gave pure iridic acid (5 g.) by the following modification of the method of de Laire and Tiemann (*loc. cit.*). To the acidified product, an equal volume of water and a little charcoal were added, and the solution was filtered, made alkaline by sodium hydroxide, saturated with carbon dioxide, extracted with ether, and again acidified. The iridic acid now obtained by extraction with ether crystallised from a little water in colourless prisms, m. p. 118°. The acid was converted into the methyl ester (5 g.; de Laire and Tiemann), which was dissolved in concentrated aqueous ammonia (*d* 0·880) and left in a closed vessel for 24 hours. The solution was evaporated, the dark sticky residue dissolved in warm alcohol, much ether added, and a dark flocculent precipitate removed by filtration. The filtrate yielded an oil which rapidly crystallised. This was dissolved in acetone, and benzene added to the hot solution, which was then treated with charcoal and filtered, and the acetone distilled off. On seeding, large, many-faced prisms slowly separated, which were again crystallised from a small quantity of water (charcoal), being thus obtained colourless and of m. p. 113° (Found: N, 6·7. $C_{10}H_{13}O_4N$ requires N, 6·6%). *Iridamide* is sparingly soluble in benzene and ether and easily soluble in alcohol and acetone. In aqueous solution it gives a weak green coloration with ferric chloride and is exceedingly readily hydrolysed to iridic acid.

Condensation of Phenylacetonitrile with Resorcinol Monomethyl Ether.—A solution of the nitrile (15 g.) and resorcinol monomethyl ether (15 g.) in ether (150 c.c.) was saturated with hydrogen chloride at 0° in presence of anhydrons zinc chloride (2·5 g.). After 48 hours, water was added and the excess of phenylacetonitrile removed in steam. The mixed ketones were dissolved in ether and shaken twice with excess of 1% aqueous sodium hydroxide. The ethereal layer yielded a residue (6·7 g.) of almost pure 2-hydroxy-4-methoxyphenyl benzyl ketone, m. p. 90° (see Tambor, *Ber.*, 1910, 43, 1884). This compound is insoluble in cold dilute alkaline solutions, and its alcoholic solution becomes red on the addition of ferric chloride. The constitution assigned to this substance by Tambor (*loc. cit.*) was confirmed by heating it for 18 hours at 180° with a large excess of acetic anhydride and about 5 times its weight of sodium acetate; it then yielded 7-methoxy-2-methyl*iso*flavone, m. p. 135·5°, identical with that prepared by the methylation of 7-hydroxy-2-methyl*iso*flavone (Part I, *loc. cit.*).

The 1% sodium hydroxide washings were acidified and extracted

with ether, and the extract was dried and distilled, yielding resorcinol monomethyl ether, b. p. 152°/20 mm., and a fraction, b. p. 260—265°/13 mm., which rapidly solidified and then crystallised from ether–ligroin in colourless granular crystals (2·1 g.), m. p. 113° (Found: C, 74·4; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%). 4-*Hydroxy-2-methoxyphenyl benzyl ketone* possesses normal phenolic properties and gives a brownish-violet ferric chloride reaction. The acetyl derivative crystallises from alcohol in diamond-shaped rhombohedra, m. p. 68°.

Condensation of Phenylacetonitrile with Orcinol Monomethyl Ether. —A solution of orcinol monomethyl ether (20 g.) and phenylacetonitrile (20 g.) in dry ether (100 c.c.) was saturated with hydrogen chloride at 0° in presence of anhydrous zinc chloride (5 g.). After 24 hours, water at 0° was added and the resulting aqueous solution of the mixed ketimines was hydrolysed on the steam-bath. Ether–benzene extracted a solid, from which the ketones were separated by fractional crystallisation from ether–ligroin. Thin, colourless, diamond-shaped plates first separated, followed by clusters of colourless needles. The two substances were sorted out and each was separately crystallised from ether–ligroin.

The plate form (2·6 g.) has m. p. 93° (Found: C, 74·9; H, 6·2. $C_{16}H_{16}O_3$ requires C, 74·9; H, 6·3%) and is 4-*hydroxy-2-methoxy-6-methylphenyl benzyl ketone*. It is exceedingly soluble in ether, alcohol, methyl alcohol, benzene, and acetone. Its alcoholic solution gives with ferric chloride a very pale yellow colour. The acetyl derivative crystallises from alcohol in thin rhombic plates, m. p. 88°.

The needles (0·4 g.) have m. p. 110° (Found: C, 75·1; H, 6·3. $C_{16}H_{16}O_3$ requires C, 74·9; H, 6·3%) and consist of 2-*hydroxy-4-methoxy-6-methylphenyl benzyl ketone*. It is much less soluble in ether than its isomeride, and gives a strong purplish-brown ferric chloride reaction. By heating at 180° for 12 hours with an equal weight of sodium acetate and excess of acetic anhydride, isolation of the product, and acetylation as before, a substance was obtained which crystallised from methyl alcohol in colourless needles, m. p. 165° (Found: C, 77·2; H, 5·9. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·8%). This substance contains no acetoxy-group, dissolves in concentrated sulphuric acid to a colourless solution exhibiting a blue fluorescence, and is therefore 7-*methoxy*-2 : 5-*dimethylisoflavone*.

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THE DYSON PERRINS LABORATORY,
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XXIII.—*Molecular Structure in Solution. Part IV. The Densities, Viscosities, and Electrical Conductivities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid at Different Temperatures.*

By Owen Rhys Howell.

The change in colour of aqueous solutions of cobalt chloride from red to blue on addition of hydrochloric acid has already been investigated by examining the physical properties at a constant temperature (20°) of two series of solutions, the one containing a fixed amount of cobalt chloride with increasing concentrations of hydrochloric acid, and the other with exactly the same concentrations of hydrochloric acid alone. By taking the differences between the values for corresponding members of the two series and plotting these against the concentration of acid, it was possible to follow the effect of the increasing acid concentration on the cobalt in solution. The densities and viscosities (J., 1927, 158), refractive indices and surface tensions (*ibid.*, p. 2039), and electrical conductivities (*ibid.*, p. 2843) were determined, and the results indicated that the effect of addition of hydrochloric acid is to throw the cobalt atom out of its association with six molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, which is red, into one with four groups or atoms, probably $CoCl_4''$, which is blue.

It was deemed of interest to examine along similar lines the exactly similar colour change which occurs when an aqueous cobalt solution is heated.

In the presence of hydrochloric acid the change of colour takes place more readily: the higher the concentration of acid, the lower the temperature at which the change occurs. In order to follow the change as far as possible into the blue region, an acidified solution was therefore chosen for the investigation.

The solution employed contained 120 g. of $CoCl_2,6H_2O$ per litre, as did the one series in the previous investigations, and it was also made 4*N* with respect to hydrochloric acid. At room temperature it is red with a distinct violet tinge and has the "muddy" appearance typical of the solutions containing both red and blue forms. At 0° it is bright red and perfectly clear and "clean"; at 60° it is blue and again quite clear.

The comparison solution was 4*N*-hydrochloric acid alone. The densities, viscosities, and electrical conductivities of these two solutions have been measured at intervals of 5° from 0° to 80°. The determinations thus extend over a range of colour about the same

as that in the previous investigations, and since the concentration of cobalt is the same in all, the results are directly comparable.

EXPERIMENTAL.

Solutions.—The solutions were prepared in the same way and from the same materials as for former investigations, and were filtered through fused Jena-glass Gooch crucibles. The concentration of acid was determined by titration against pure dry sodium carbonate, and the concentration of cobalt chloride was checked by estimating the total chlorine in the solution gravimetrically as silver chloride. All concentrations were determined at 18°.

Temperature Control.—All measurements were made in a gas-regulated thermostat with a glass front and back. For the higher temperatures the water was covered with a layer of high-boiling paraffin.

Temperatures below atmospheric were obtained in what is believed to be a novel manner. A stream of water from the mains was run through a constant-level device to secure a fixed head and thence through a copper coil cooled in ice. The steady stream of ice-cold water thus obtained was led through a similar coil immersed in the water filling the thermostat and then discharged into it, the thermostat being fitted with a constant-level arrangement for overflow. In this manner a perfectly even and easily regulated cooling effect was applied to the thermostat, similar to that caused by radiation from thermostats at temperatures above atmospheric. It was counterbalanced by the gas flame working through the regulator in the usual way, and the temperature could be kept constant to within $\pm$ 0·02° as easily as at higher temperatures.

Two standard thermometers were employed, newly calibrated at the National Physical Laboratory to the nearest 0·05°.

Determination of Density.—Densities were determined as in previous investigations with a bottle of about 25 c.c. capacity made of Pyrex glass. For temperatures below atmospheric and also above 60°, a pyknometer was employed. The values adopted for water were those of Thiesen (Landolt and Börnstein, "Tabellen," 1923, 73). For the highest temperatures there may be an error of one unit in the last place of decimals; for the others, it is less than this.

Determination of Viscosity.—Viscosities were determined by means of viscometers of the form previously described. For this series of measurements, they were made of Pyrex glass and were found to be effective in preventing loss through evaporation. The time of flow was taken by means of a stop-watch reading to 0·1 sec., and was reproducible to within this limit in every determination.

Since the minimum time of flow in the whole series was 240 seconds, the results are correct to within 0·1%.

The values for the viscosity of water at different temperatures given by various observers are not in good agreement. The values used here are the means of those of Hosking (*Phil. Mag.*, 1909, **17**, 502; **18**, 260) and of Bingham and White (*Z. physikal. Chem.*, 1912, **80**, 670) up to 25°; beyond 25°, Hosking gives his results to only three significant figures, and those of Bingham and White are therefore taken, except for 60°, where the given value is evidently too high and the mean is again accepted.

Determination of Conductivity.—Electrical conductivities were determined in the cell already described (*loc. cit.*). For every determination at least four different resistances were used in the circuit, the mean point of balance was taken after several trials, and the conductance of the cell calculated for each. The values were in every instance within 0·1% of the mean.

The cell constant was determined by using *N*-potassium chloride solution prepared from the pure dried salt (Kahlbaum's). Determinations were made at each working temperature from 0° to 25°, over which range the conductivity of this solution is known (Kohlrausch, Holborn, and Diesselhorst, *Wied. Ann.*, 1898, **64**, 417), and almost identical values were obtained for the cell constant. Calculations from the dimensions of the cell showed that the variation over the whole range of temperature should be less than 0·05%, and therefore the mean of the values obtained experimentally was used for all the estimations.

Results.

Densities.—The densities of the two solutions (cobalt chloride with 4*N*-hydrochloric acid, and 4*N*-acid alone) are given in cols. 2 and 4 respectively of Table I. The results at 20°, *viz.*, 1·1209 and 1·0657, are almost identical with those interpolated for the same solutions from the previous investigation, *viz.*, 1·1209 and 1·0656, respectively. The densities are plotted against the temperature in Fig. 1. It is seen that both curves are perfectly smooth and continuous. They are both represented by an equation of the form $d_{t°} = d_{0°}(1 - \alpha t - \beta t^2)$, where α and β are constants. The values of the constants for the two solutions are:

$$CoCl_2 + HCl: \alpha = 307 \times 10^{-6};\ \beta = 140 \times 10^{-8};$$
$$HCl\ alone: \alpha = 289 \times 10^{-6};\ \beta = 142 \times 10^{-8};$$

and the calculated values are given in cols. 3 and 5 respectively. It is seen that the agreement between the observed and the calculated values is very fair; the maximum difference is two units

in the last place of decimals, and the average difference is less than one unit in both series.

The density differences (*i.e.*, the differences between the observed densities of the two solutions at each temperature) are given in col. 6 of Table I, and are plotted against the temperature in Fig. 1. The curve is quite smooth and continuous (see later).

TABLE I.

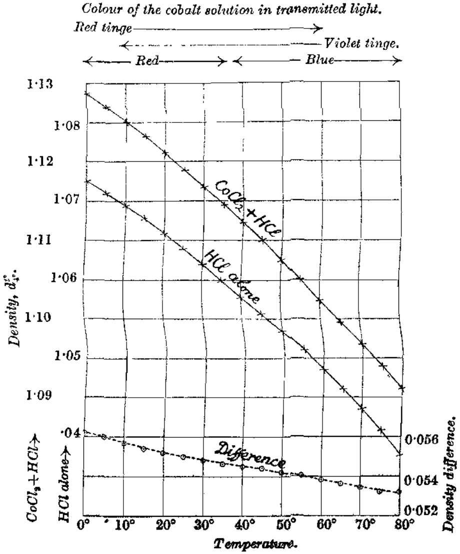
1.	2.	3.	4.	5.	6.
	Density, $d_{4°}^{t°}$.				
	$CoCl_2 + HCl$,		HCl alone,		
Temp.	obs.	calc.	obs.	calc.	Difference (2—4).
0°	1·1287	1·1287	1·0725	1·0725	0·0562
5	1·1269	1·1269	1·0709	1·0709	0·0560
10	1·1250	1·1251	1·0693	1·0693	0·0557
15	1·1231	1·1231	1·0677	1·0675	0·0554
20	1·1209	1·1211	1·0657	1·0657	0·0552
25	1·1188	1·1190	1·0638	1·0638	0·0550
30	1·1167	1·1169	1·0619	1·0618	0·0548
35	1·1144	1·1146	1·0598	1·0598	0·0546
40	1·1122	1·1123	1·0577	1·0577	0·0545
45	1·1100	1·1099	1·0556	1·0555	0·0544
50	1·1075	1·1074	1·0533	1·0532	0·0542
55	1·1050	1·1049	1·0510	1·0509	0·0540
60	1·1021	1·1022	1·0483	1·0484	0·0538
65	1·0995	1·0995	1·0459	1·0459	0·0536
70	1·0967	1·0967	1·0433	1·0433	0·0534
75	1·0940	1·0938	1·0408	1·0407	0·0532
80	1·0910	1·0909	1·0378	1·0380	0·0532

TABLE II.

1.	2.	3.	4.	5.	6.
	Viscosity coefficient, $\eta_{t°}$.				
	$CoCl_2 + HCl$,		HCl alone,		
Temp.	obs.	calc.	obs.	calc.	Difference (2—4).
0°	0·02358	0·02358	0·01958	0·01958	0·00400
5	0·02077	0·02077	0·01729	0·01727	0·00348
10	0·01842	0·01845	0·01533	0·01535	0·00309
15	0·01647	0·01650	0·01375	0·01375	0·00272
20	0·01486	0·01486	0·01241	0·01241	0·00245
25	0·01345	0·01346	0·01125	0·01126	0·00220
30	0·01225	0·01226	0·01028	0·01028	0·00197
35	0·01120	0·01122	0·009419	0·009419	0·001781
40	0·01031	0·01031	0·008649	0·008672	0·001661
45	0·009519	0·009503	0·008012	0·008014	0·001507
50	0·008821	0·008793	0·007443	0·007431	0·001378
55	0·008191	0·008164	0·006923	0·006916	0·001268
60	0·007608	0·007602	0·006448	0·006455	0·001160
65	0·007102	0·007097	0·006041	0·006040	0·001061
70	0·006654	0·006643	0·005667	0·005667	0·000987
75	0·006218	0·006234	0·005321	0·005329	0·000897
80	0·005844	0·005861	0·005003	0·005021	0·000841

Viscosities.—The viscosities of the two solutions are given in Table II, cols. 2 and 4, and plotted against temperature in Fig. 2 : both curves are again smooth and continuous. The results at 20°, *viz.*, 0·01486 and 0·01241, may be compared with those calculated for the same solutions from the results obtained in previous investigations, *viz.*, 0·01487 and 0·01240, respectively.

FIG. 1.

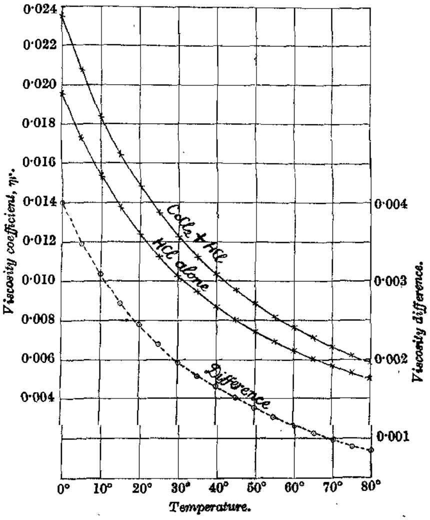


Many equations have been suggested by different observers to express the relation between viscosity and temperature. Most of them give good agreement for non-associated, but not for associated liquids. The most satisfactory (see Thorpe and Rodger, *Phil. Trans.*, 1894, *A*, **185**, 397) is the second expression proposed by Slotte (*Beibl.*, 1892, **16**, 182), *viz.*, $\eta_t = \eta_0/(1+\beta t)^n$, which has been shown to reproduce the observed values for non-associated

liquids with great accuracy over wide ranges of temperature and to give good agreement for many associated liquids also. It is now shown that the equation also applies to solutions, even to those containing complexes.

The equation is preferably written in the form $\eta_{t_1}/\eta_{t_2} = [(t_1 + k)/(t_2 + k)]^{-C}$, where k and C are constants. It is most conveniently applied to a series of values over a wide range of temperature by

FIG. 2.

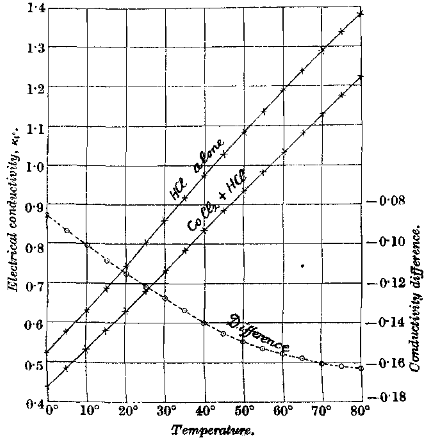


plotting the logarithms of the viscosities against the logarithms of $(t + k)$ for different values of k. A few attempts soon fix that value of k which gives a perfectly straight line, and the slope of this line gives C. The calculated values are then readily obtained from the expression $\log \eta_t = K - C \log (t + k)$, where $K = \log \eta_0 + C \log k$. The values of the constants (k being given only to the nearest whole number) for the two solutions are

$CoCl_2$ + HCl : $k = 68$; $C = 1·790$;
HCl alone : $k = 64$; $C = 1·678$;

and the calculated viscosities are given in cols. 3 and 5 of Table II. It is seen that the agreement is very good; the maximum deviations are 0·34% and 0·27%, and the average deviations only 0·15% and 0·08% in the two series, respectively. Still more concordant values would doubtless result if the accepted viscosities for water were more trustworthy and if slight adjustments were made in the constants. The viscosity differences are given in col. 6 of Table II and are plotted against the temperature in Fig. 2; the curve is smooth and continuous (*vide infra*).

FIG. 3.



Electrical Conductivities.—The conductivities of the two solutions are given in Table III, cols. 2 and 4. The results at 20° may be compared with those for the same solutions read from the curves obtained in the previous investigations; the figures are 0·6287 and 0·7440, as against 0·6290 and 0·7430. The result for hydrochloric acid at 25°, 0·8014, agrees well with that of Green (J., 1908, 93, 2023), who found 0·8016 for the same solution.

The conductivities are plotted against temperature in Fig. 3, and it is seen that both curves are again quite smooth and continuous. They may both be represented by an equation of the

TABLE III.

1.	2.	3.	4.	5.	6.
	Electrical conductivity, κ_{t°.				
	$CoCl_2$ + HCl,		HCl alone,		
Temp.	obs.	calc.	obs.	calc.	Difference (2—4).
0°	0·4360	0·4360	0·5217	0·5217	−0·0857
5	0·4827	0·4827	0·5766	0·5763	−0·0939
10	0·5310	0·5306	0·6318	0·6319	−0·1008
15	0·5788	0·5794	0·6873	0·6881	−0·1085
20	0·6287	0·6290	0·7440	0·7449	−0·1153
25	0·6795	0·6792	0·8014	0·8018	−0·1219
30	0·7310	0·7297	0·8587	0·8589	−0·1277
35	0·7818	0·7806	0·9157	0·9157	−0·1339
40	0·8317	0·8315	0·9719	0·9722	−0·1402
45	0·8823	0·8822	1·028	1·028	−0·1457
50	0·9334	0·9328	1·083	1·083	−0·1496
55	0·9818	0·9827	1·135	1·137	−0·1532
60	1·032	1·032	1·188	1·189	−0·156
65	1·080	1·081	1·238	1·240	−0·158
70	1·128	1·129	1·280	1·289	−0·161
75	1·175	1·175	1·337	1·337	−0·162
80	1·222	1·220	1·385	1·382	−0·163

form $\kappa_{t^\circ} = \kappa_{0^\circ}(1 + \alpha t + \beta t^2 - \gamma t^3)$, where α, β, and γ are constants. The values of the constants for the two solutions are

$CoCl_2$ + HCl : $\alpha = 0{\cdot}02116$; $\beta = 5915 \times 10^{-8}$; $\gamma = 5320 \times 10^{-10}$;
HCl alone : $\alpha = 0{\cdot}02073$; $\beta = 4442 \times 10^{-8}$; $\gamma = 5748 \times 10^{-10}$;

and the calculated conductivities are given in cols. 3 and 5, respectively, of Table III. It is seen that the agreement is very good; the maximum deviations are 0·19% and 0·18%, respectively, and the average deviation is only 0·07% in each series. The conductivity differences are given in col. 6 of Table III and are plotted against the temperature in Fig. 3. It is seen that the curve is smooth and continuous (*vide infra*).

Discussion of Results.

In the previous series of experiments (*loc. cit.*) on the effect of the addition of hydrochloric acid to cobalt chloride in solution, the curves for the solutions of hydrochloric acid alone were all smooth and continuous and could be represented by comparatively simple expressions, but those for cobalt chloride with hydrochloric acid exhibited discontinuity, the differences curves being characterised by marked inflexion.

Thus, the density-differences curve exhibited a point of inflexion; the density difference at the concentration of acid at which the inflexion occurs, as read from the line joining the values at the extreme ends of the series, is 0·0503, whereas the actual value is 0·0544, which is 8% greater. Similarly, the viscosity-differences

curve exhibited a maximum; the difference read from the straight line is 0·00182, and the actual value is 0·00276, which is 51% higher. Again, the conductivity differences curve exhibited a minimum, the differences being respectively + 0·0095 and − 0·1230, which is 1395% lower.

In this series of experiments, on the other hand, the curves for these three properties of the solutions of hydrochloric acid both alone and with cobalt chloride are smooth and may be represented with nearly equal accuracy by simple expressions. Consequently the differences curves are also smooth. It follows that, although the colour change on the addition of hydrochloric acid to cobalt chloride solution and that on heating the solution appear precisely similar, the mechanism underlying the change is profoundly different.

The curves obtained in the previous investigations could be interpreted only on the hypothesis that on continued addition of hydrochloric acid to the cobalt chloride solution, the positively charged cobalt ions were progressively converted into negatively charged complex ions and that the point of inflexion (maximum or minimum) on the differences curves occurred when equal numbers of each were present and the attraction between them was consequently greatest.

Since all the curves obtained in the present investigation are smooth, it follows that there is no change (or, at most, a negligibly small change) in the numbers of oppositely charged cobalt ions. The mechanism of the colour change which occurs on cooling or heating these acid solutions must therefore be different from that brought about by alteration of acid concentration (see above), and must be explained by the addition or subtraction, respectively, of two groups to or from each kind of ion without changing its charge. This can be effected only by addition or subtraction of water molecules, and the phenomenon is therefore one of hydration and dehydration according to the scheme

$$\text{Red}\left\{\begin{array}{c} Co(H_2O)_6^{\cdot\cdot} \rightleftharpoons Co(H_2O)_4^{\cdot\cdot} \\ CoCl_4(H_2O)_2'' \rightleftharpoons CoCl_4'' \end{array}\right\}\text{Blue} \qquad \left(\xrightarrow{\text{heating}},\ \xleftarrow[\text{cooling}]{}\right)$$

The first explanation suggested to account for the change of colour of cobalt solutions, not only on heating, but also on addition of alcohol, acid, and certain salts, was that of hydration (von Babo, *Jahresber.*, 1857, 72; Schiff, *Annalen*, 1859, 110, 203). Many investigations on the absorption spectra of cobalt solutions

led to the same conclusion (Russell, *Proc. Roy. Soc.*, 1881, **32**, 258; Hartley, *Trans. Roy. Dublin Soc.*, 1900, **7**, 253; J., 1903, **83**, 401; Jones and Uhler, *Amer. Chem. J.*, 1907, **37**, 126), and the formation of definite aquo-complexes has been postulated (Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273; **166**, 237; Gróh and Schmid, *ibid.*, **162**, 321).

The present investigations, however, show that the mechanism of the change of colour on addition of acid is different from that on heating, yet the two are explained and harmonised on the general theory of colour based on the number of groups surrounding the cobalt atom (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833; compare Hantzsch and Shibata, *Z. anorg. Chem.*, 1912, **73**, 309; Hantzsch, *loc. cit.*).

It may be noted that this work shows that not only the kation but also the complex anion is hydrated. Indeed, with a solution containing approximately equal numbers of the two kinds of ions, the change of colour to red (hydration chiefly of the anion) on cooling is far more rapid than the change to blue (dehydration of the kation) on heating.

Although the differences curves obtained on addition of hydrochloric acid to cobalt chloride solution differ essentially in form from those obtained on heating the solution, there is one feature in which they all resemble one another, namely, that they all tend eventually to become parallel to the axis of acid concentration or of temperature, showing that the change of the cobalt atom to the blue configuration is nearing completion. No further change being then possible, the physical properties of the cobalt solution compared with those of the acid alone become and remain constant. It is evident from the form of the curves obtained in this work, that dehydration of the cobalt ions would not be complete even at 100°.

Summary.

1. The densities, viscosities, and electrical conductivities of two aqueous solutions, one containing 120 g. of $CoCl_2,6H_2O$ per litre with hydrochloric acid ($4N$) and the other hydrochloric acid ($4N$) alone, have been determined at intervals of 5° from 0° to 80° and plotted against the temperature.

2. The curves of each of the properties are smooth for both the solutions and expressions have been found for them which give good agreement with the observed values.

3. The three differences curves are also smooth, unlike those obtained on continued addition of hydrochloric acid to cobalt chloride solution at constant temperature.

4. It is therefore concluded that the relative number of oppositely

charged cobalt ions in the solution is unchanged over the whole range of temperature and therefore during the colour change.

5. Since the colour is determined by the number of groups surrounding the cobalt atom, it follows that the change must be due to addition and subtraction of water molecules, leaving the charge of the ion unaltered.

6. The change of colour is therefore due to hydration and dehydration on cooling and heating respectively.

7. Both kation and anion are hydrated, gaining or losing two molecules of water on cooling or heating respectively, so that the total number of groups surrounding the cobalt atom is six when red and four when blue.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, September 17th*, 1928.]

XXIV.—*Properties of Conjugated Compounds. Part VI. The Dibromination Products of Cyclic Butadienes.*

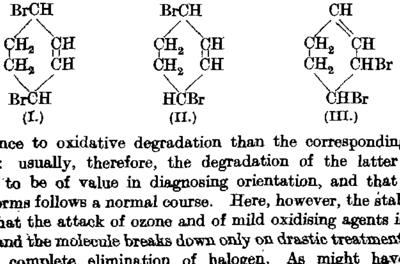
By ERNEST HAROLD FARMER and WILLIAM DALLAS SCOTT.

IN foregoing papers of this series it has been pointed out that the migratory changes displayed by the dibromides of butadienoid hydrocarbons are fundamentally based on the propenoid change C:C·C ⟶ C·C:C. The facile production of 1 : 4-, 1 : 6-, etc., compounds by isomerisation of the corresponding 1 : 2-forms suggests the possibility that all such derivatives of simple conjugated compounds may originate in addition at a single ethylenic linkage and not, wholly or partly, as the result of differential tendencies inherent in the butadienoid structure. It is sought, in continuing the examination of hydrocarbon addition products, to accumulate evidence entirely consistent with additive attack at a single ethylenic centre (whether the mechanism of differential orientation prove finally to be ionic in character or otherwise), and it is shown in this paper that in one instance investigated, namely, that of $\Delta^{1:3}$-*cyclo*hexadiene, this is actually the case. It is reasonable to assume that, in other cases where the issue is not so clear, the lack of definite evidence is due to failure to discover the correct experimental conditions which will enable the 1 : 2-products to be isolated.

Bromination of $\Delta^{1:3}$-cyclo*Hexadiene*.—When $\Delta^{1:3}$-*cyclo*hexadiene is dibrominated in hexane or chloroform below −15° and the solvent is removed immediately, without application of heat, a mixture of two isomeric dibromides—a liquid and a solid—is obtained. Each of

these substances passes readily into a third solid isomeride at room temperature or, more rapidly, on heating. The isomerisation of the original solid form is slow in the dry state (requiring several weeks), that of the liquid more rapid (8% at 15° in 25 hours, 40% at 100° in 15 minutes); both forms change readily when dissolved in a solvent. If there is delay in working up the bromination product, or if the temperature of the mixture is raised, as, for instance, by distilling off the solvent, partial disappearance of the original forms may occur: indeed the solid form at least may disappear so completely as to become undetectable. The proportion in which the original bromides appear varies little with the nature of the solvent or with the degree of dilution.

The third isomeride (identical with the *cyclo*hexadiene dibromide obtained by Crossley and Haas, J., 1903, **83**, 498; 1904, **85**, 1403, and by Zelinsky and Gorsky, *Ber.*, 1908, **41**, 2428) is purely a derived form and doubtless represents one of the stereoisomeric forms (I and II). 1 : 4-Dibromides always display a much greater



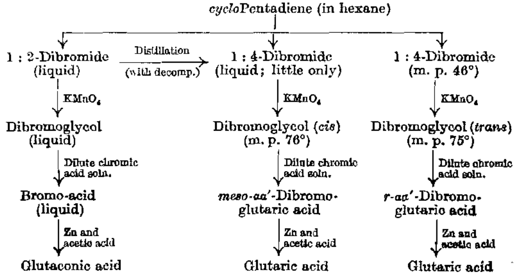
(I.) (II.) (III.)

resistance to oxidative degradation than the corresponding 1 : 2-forms: usually, therefore, the degradation of the latter is too severe to be of value in diagnosing orientation, and that of the 1 : 4-forms follows a normal course. Here, however, the stability is such that the attack of ozone and of mild oxidising agents is withstood and the molecule breaks down only on drastic treatment which causes complete elimination of halogen. As might have been anticipated, attempts to convert this dibromide into its diethoxy-derivative with sodium ethoxide resulted only in the production of benzene. The two original bromides are attacked by ozone and by permanganate so readily that control of degradation is difficult. With the latter reagent the corresponding dibromoglycols are produced in small yield, but the further oxidation cannot be arrested before bromine is eliminated from the molecule. There can be little doubt, however, that the bromides represent stereoisomeric 1 : 2-forms (III).

Bromination of cyclo*Pentadiene*.—Thiele's investigation of the dibromination of *cyclo*pentadiene (*Annalen*, 1900, **314**, 296) indicates that only 1 : 4-forms are produced; by bromination in chloroform solution, distillation of the solvent, and fractionation of the bromide

mixture under reduced pressure, he obtained a liquid and a solid *cyclo*pentadiene dibromide; since these were oxidised *via* their respective dibromoglycols to *meso* and *racemic* forms of αα′-dibromoglutaric acid, their 1 : 4-orientation was definitely demonstrated. With the greater part of Thiele's statement we are in complete agreement; if, however, isomerisation during the isolation of dibromides is guarded against, not only is 1 : 4-bromination found to be partial, but interesting dilution and solvent effects on the quantitative relation between the 1 : 2-form and its 1 : 4-isomerides become apparent.

The incidence of the bromination products obtained in *n*-hexane below −15° is shown in the following scheme. The details concerning the degradation products of the two 1 : 4-isomerides are identical with those already given by Thiele. It is also fairly certain that on distillation the liquid 1 : 2-dibromide is converted (with degradation) to a small extent into the solid 1 : 4-form :



preferentially, however, it yields the liquid isomeride. In hexane solution, with increasing dilution the proportion of solid 1 : 4-dibromide isolated from the bromination mixture steadily diminishes, falling, *e.g.*, from 40% to 12% as the final total bromide content increases from 0·28 g. to 2 g. per c.c. of solvent. The effect of substituting chloroform for hexane is drastically to reduce the proportion of solid 1 : 4-form and to increase the total proportion of 1 : 4-dibromide in the bromination product.

Experimental.

Bromination of $\Delta^{1:3}$-cyclo*Hexadiene.*—The *cyclo*hexadiene was prepared by Hofmann and Damm's method (*Schleischen Kohlenforsch. Kaiser Wilhelm Ges.*, 1925, **2**, 97) from pure *cyclo*hexene and

fractionated over sodium in a stream of carbon dioxide; it had b. p. 80°, $n^{16\cdot0°}$ 1·4760, $d_4^{16\cdot0°}$ 0·8421; whence $[R_L]_D$ =26·806.

The bromination was carried out in a flask fitted with a dropping-funnel, a calcium chloride tube, and a stirrer and immersed in a freezing mixture. Usually 8 g. of the hydrocarbon, dissolved in chloroform or, preferably, *n*-hexane, were brominated at one time. When the theoretical quantity of bromine (diluted) had been added with constant stirring, the solvent was removed as quickly as possible by means of a good vacuum pump, a little light petroleum added to the residue, and the solid bromination product *immediately* separated by strong cooling and filtration. Careful repetitions of the "freezing-out" process and final removal of the solvent (under reduced pressure) from the residual liquor yielded a colourless liquid dibromide.

1 : 2-*Dibromo*-Δ^3-cyclo*hexene* (III). The solid dibromide, after being washed with light petroleum, was usually pure and formed colourless prisms, m. p. 68° (Found : Br, 66·6. $C_6H_8Br_2$ requires Br, 66·6%). Whenever there was delay (for instance, postponement over-night) in isolating the bromination products, in separating the solid dibromide from its liquid isomeride, or in removing crystals of dibromide from a crystallising medium, the m. p. of the crystals obtained was usually about 54° : from such crystals, by rapid fractional crystallisation from light petroleum, small quantities of an isomeric 1 : 4-dibromide, m. p. 108° (see below), could be separated. If the delay in isolating the bromination products was prolonged, there was partial or complete replacement of the solid 1 : 2-dibromide by its isomeride, m. p. 108°.

The liquid dibromide, immediately after isolation, appeared to be free from impurity other than residual traces of its solid stereoisomeride (Found : Br, 66·4%).

1 : 4-Dibromo-Δ^2-*cyclo*hexene was the sole solid product isolated when there was a delay of 3 days in working up the dibromination mixture, or when heat was applied in the removal of the bromination diluent. It was also directly obtained from the two pure 1 : 2-dibromo*cyclo*hexenes (see below). It crystallised from light petroleum in colourless prisms, m. p. 108° (Crossley and Haas, *loc. cit.*, give m. p. 108—109°) (Found : Br, 66·7%).

Isomerisation of 1 : 2-*Dibromo*cyclo*hexene*.—The pure *solid* dibromide suffered gradual isomerisation on standing : after several weeks, complete conversion into 1 : 4-dibromo*cyclo*hexene had occurred. Isomerisation appeared to be accelerated when the dibromide was dissolved in hexane or chloroform and became rapid when the pure dibromide or its solutions were heated.

The *liquid* dibromide isomerised gradually at room temperature and more rapidly on heating; at 0°, change became perceptible after

2—3 days. The possibility of reversing the 1 : 2- ⟶ 1 : 4-change at 100° could not be gauged owing to the degradation of the 1 : 4-dibromide when heated for a prolonged period : if the reverse change occurs, it is very slow. On distillation, isomerisation was rapid, the boiling point steadily rising from about 75° to 120°/2 mm.; the fraction of b. p. 110—120°/2 mm., which solidified on cooling, was almost pure 1 : 4-dibromo*cyclo*hexene.

*Oxidation of the Isomeric Dibromo*cyclo*hexenes*.—The stability of the 1 : 4-dibromide, m. p. 108°, frustrated all attempts to oxidise it with permanganate at 0° or at room temperature. The finely powdered bromide was unattacked by cold aqueous chromic acid, but was converted by the hot reagent into succinic acid. The action of ozone was very slow : the bromide suffered change after prolonged ozonisation, but no satisfactory decomposition of the product could be achieved. Nitric acid was equally unsatisfactory as an oxidising agent.

The 1 : 2-dibromide, m. p. 68°, was fairly readily oxidised by permanganate at 0° to the corresponding dibromoglycol, but much of the latter compound suffered further oxidation before the first stage of oxidation was complete. To an acetone solution of 6 g. of the bromide, 60 c.c. of an aqueous solution of permanganate and magnesium sulphate (5% of each) were very slowly added. The manganese mud was filtered off and all acetone removed from both mud and filtrate in a rapid current of air. The mud, suspended in a little water, was just brought into solution by addition of sulphuric acid and sodium bisulphite. The solution, after filtration of a large quantity of unchanged dibromide, was combined with the acetone-free filtrate and extracted ten times with alcohol-free ether. The extract, freed from acid matter by cautious agitation with a few c.c. of saturated bicarbonate solution, was thoroughly dried with sodium sulphate. After evaporation of the ether the residue, 1 : 2-*dibromo*-3 : 4-*dihydroxy*cyclo*hexane*, solidified completely. It separated from petroleum (b. p. 60—80°) in colourless prisms, m. p. 96—98° (Found : Br, 58·1. $C_6H_{10}O_2Br_2$ requires Br, 58·3%). The yield was about 25%, calculated on the bromide taken.

The liquid 1 : 2-dibromide, on oxidation in a similar manner, gave a syrupy glycol containing traces of the above-described dibromoglycol. The latter was extracted with petroleum, but since the liquid glycol decomposed on distillation complete purification could not be effected. The complementary acidic portion of the oxidation product consisted largely of succinic acid.

*Oxidation of the Isomeric Dibromodihydroxy*cyclo*hexanes*.—The most careful treatment with cold aqueous chromic acid or with neutral permanganate failed to prevent loss of bromine, and the

product was invariably succinic acid; no $\alpha\alpha'$-dibromoadipic acid could be obtained.

Bromination of cyclo*Pentadiene.*—The dimeride required for the generation of the hydrocarbon was worked up from " aged " benzene forerunnings as described by Perkins and Cruz (*J. Amer. Chem. Soc.*, 1927, **49**, 517). The carefully fractionated dimeride from certain batches of forerunnings solidified with difficulty on cooling and the crystals, after recrystallisation from alcohol (an operation accomplished with difficulty owing to great solubility), always melted at 19°. The dimeride from other batches was almost completely solid at room temperature and the crystals, which separated easily from strongly cooled alcoholic solution, melted at 32°. The former of these compounds possibly represents a homogeneous modification corresponding to that isolated by Staudinger and Rheiner (*Helv. Chim. Acta*, 1924, **7**, 23) from the intensely cooled liquid portion of commercial di*cyclo*pentadiene. The boiling points of both the lower- and the higher-melting portion were identical (56°/13 mm.); there was no portion boiling above this temperature as recorded by Staudinger and Rheiner. Wieland and Bergel (*Annalen*, 1925, **446**, 19), who separated a liquid dimeride fraction from the di*cyclo*pentadiene, m. p. 32·5°, also give the b. p. 56°/13 mm. for both portions and state that they could find no trace of Staudinger and Rheiner's " isomeric di*cyclo*pentadiene, b. p. 68—70°/12 mm."

Both the lower- and the higher-melting portion of the dimeride yielded *cyclo*pentadiene when heated with iron filings at 185—190° in the usual way. For the bromination experiments the hydrocarbon was redistilled once (b. p. 42°), precautions being taken to prevent access of moisture.

Bromination in n-*hexane*. Bromination was effected at the temperature of an ice–salt bath, as described above. A deficiency of bromine was always employed in additions to *cyclo*pentadiene and the yields were calculated on the amount of bromine taken. When addition was complete, a solid bromination product was directly frozen out in the usual way. This corresponded to Thiele's *trans*-1 : 4-dibromo-Δ^2-*cyclo*pentene, m. p. 45—46° (Found : Br, 70·9. Calc. : Br, 70·8%). Yield, 40%. Removal of the solvent left an almost colourless liquid consisting mainly of 1 : 2-*dibromo*-Δ^3-*cyclo*-*pentene*, d^{20° 1·8867 (Found : Br, 70·6. $C_5H_6Br_2$ requires Br, 70·7%), but containing, as shown by oxidation experiments, a small proportion of *cis*-1 : 4-dibromo-Δ^2-*cyclo*pentene.

Variation of the proportion of diluent employed during bromination affected considerably the amount of the solid dibromide that could be frozen out. The following approximate figures show the relation between the amount of solid isolated and the concentration

of total dibromide (g. per c.c. of solvent employed) in the bromination mixture.

Concentration	0·27	0·47	0·67	1·25	2·00
Solid dibromide, %	40·0	27·8	27·1	24·0	11·6

Bromination in chloroform. This was effected at the temperature of an ice–salt bath and all precautions against rise in temperature, etc., were taken. The faintly yellow product darkened rapidly as the solvent was removed. On dilution of the chloroform-free product with light petroleum, and strong cooling, less than 2% of solid dibromide could by any means be induced to separate. The dark-coloured liquid dibromide which remained when the solvent was removed was a mixture of 1 : 2-dibromo-Δ^3-*cyclo*pentene and *cis*-1 : 4-dibromo-Δ^2-*cyclo*pentene.

Isomerisation of cyclo*PentadieneDibromides.*—The liquid dibromide ($d^{20°}$ 1·8977) obtained from chloroform solutions of the hydrocarbon distilled witb considerable decomposition. The product was a pale yellow liquid (b. p. 68—80°/5 mm.; yield, 82%) which could be redistilled with only slight decomposition. When, in the first distillation, the highest-boiling fraction was retained in the distilling flask and extracted with petroleum, crystals of the solid dibromide, m. p. 45°, were obtained (yield, less than 10%). It is not certain to what extent this was formed during distillation: the solid dibromide is apparently much more soluble in the corresponding liquid 1 : 4-dibromide than in its liquid 1 : 2-isomeride and some proportion of this yield is possibly attributable to incomplete separation at the outset. After several distillations a stable, constant-boiling fraction, b. p. 72°/5 mm., 82°/15 mm., $d^{20°}$ 1·9198 (Found: C, 26·6; H, 2·7; Br, 70·8. Calc.: C, 26·6; H, 2·7; Br, 70·8%), was obtained which behaved on oxidation as nearly pure *cis*-1 : 4-dibromo-Δ^2-*cyclo*hexene (compare Thiele, *loc. cit.*). In view of the evidence furnished by oxidation of the differently derived liquid dibromides, there is every indication that the decomposition which attends the first fractionations is entirely attributable to the presence of the lower-boiling 1 : 2-dibromo-Δ^3-*cyclo*hexene, which, on heating, changes into its liquid 1 : 4-isomeride but largely suffers degradation. When the chloroform solution of the bromination product is worked up as described by Thiele, some of the 1 : 2-dibromide appears to suffer isomerisation in the boiling chloroform and the subsequent decomposition during fractionation is lessened.

When the analytically pure liquid obtained by brominating the hydrocarbon in hexane solution was heated at 100° at ordinary pressure, or distilled at reduced pressure, the decomposition was very great. Usually about 45% of the bromide escaped degradation at low pressures, yielding a non-homogeneous liquid, b. p. 65—74°/5 mm.,

This liquid on further fractionation yielded pure *cis*-1 : 4-dibromo*cyclo*hexene, some proportion of which (see below) was present as such as the outset.

Oxidation of trans-1 : 4-*Dibromo*-Δ^2-cyclo*pentene*.—This and the succeeding oxidations of the *cyclo*pentadiene dibromides were conducted in essentially the way already described. In this case the employment of 12·9 g. of the bromide, 120 c.c. of 5% permanganate solution and excess of magnesium sulphate gave a 52% yield of *trans*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, m. p. 75° (Found : Br, 61·6. Calc.: Br, 61·5%). This substance, when further oxidised by cold aqueous chromic acid (compare Thiele, *loc. cit.*), gave an 85% yield of *r*-$\alpha\alpha'$-dibromoglutaric acid, m. p. 142° (Found : Br, 55·3. Calc.: Br, 55·1%).

Oxidation of cis-1 : 4-*Dibromo*-Δ^2-cyclo*pentene*.—The *cis*-bromide (6·8 g.), treated with 83 c.c. of 5% neutral permanganate solution, gave an 80% yield of crude dibromoglycol, which consisted mainly of *cis*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, m. p. 76° (mixed m. p. with the corresponding *trans*-glycol, 45—50°), but contained a quantity of syrupy glycol, presumably the isomeric 1 : 2-dibromo-compound. The former substance on further oxidation by Thiele's method gave *meso*-$\alpha\alpha'$-dibromoglutaric acid, m. p. 170° (Found : Br, 55·5. Calc. : Br, 55·1%). The crude glycol when similarly oxidised gave this acid contaminated with a syrupy bromo-acid. Both dibromoglutaric acids yielded glutaric acid when reduced with zinc and acetic acid as recorded by Thiele.

Oxidation of 1 : 2-*Dibromo*-Δ^3-cyclo*pentene*.—The liquid dibromide (24·8 g.) obtained by brominating *cyclo*pentadiene in hexane, when treated with 5% neutral permanganate solution (23 c.c.), gave a 47% yield of a water-soluble, non-solidifiable, syrupy glycol. This substance, from which none of the isomeric dibromoglycols could be separated, decomposed on distillation and could not be further purified. It was further oxidised by aqueous chromic acid, during which (as during oxidation to the glycol stage) much of the material suffered severe degradation. From the syrupy acid so obtained, a very small amount of *meso*-$\alpha\alpha'$-dibromoglutaric acid was readily separated; the remainder did not solidify and was directly debrominated with zinc dust and acetic acid. From the product a mixture of glutaconic acid and non-solidifiable acidic material was obtained; the yield, however, of the former was only small and all attempts to decrease the degradation during oxidation of the 1 : 2-dibromide failed.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Chemical Society

for grants which have defrayed a considerable portion of the cost of the investigation; and also to the Gas Light and Coke Company for gifts of crude hydrocarbon.

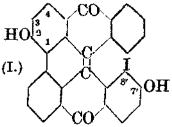
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, November 9th*, 1928.]

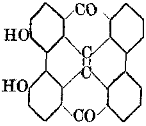
XXV.—*Reduction Products of the Hydroxyanthraquinones. Part X.*

By RICHARD WALTER HARDACRE and ARTHUR GEORGE PERKIN.

WHEN 3-hydroxyanthranol is gently oxidised, the corresponding dihydroxydianthrone is produced, and from this the dihydroxydianthraquinone and dihydroxyhelianthrone can be successively obtained by similar methods (Haller and Perkin, J., 1924, **125**, 239; Perkin and Yoda, J., 1925, **127**, 1881). The last substance, by iodination in pyridine solution, readily yields a well-characterised monoiodo-derivative, a fact which suggested that the two hydroxyls present are not similarly situated. Therefore, although this compound, judging from its method of formation, could be either a 2 : 2′-, 2 : 7′- or 7 : 7′-dihydroxyhelianthrone, constitution (I) was preferred, the iodine presumably entering position 8′.*

(I.)



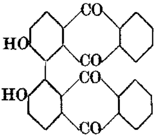
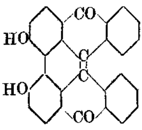


(II.)

More recently it has been found that by a more drastic treatment of the dihydroxyhelianthrone with iodine in pyridine solution a di-iodo-compound can be prepared (bromine reacts similarly)—a behaviour which, indicating as it does some resistance to the entry of a second iodine atom, harmonises with the view expressed above. On the other hand, experiment has now definitely shown that the iodine atom in monoiododihydroxyhelianthrone is not in position 8′, because, on exposure of its acetyl derivative in benzene solution to sunlight, the iododiacetoxynaphthadianthrone is produced. Such a reaction could not occur in the case of (I) without elimination of iodine (II) and it is thus evident that the halogen atom or atoms have entered β-positions.

* In the former communication (H. and P., p. 233) this was termed 5′-iodo-3 : 6′-dihydroxyhelianthrone, the orientation employed being that in vogue with anthraquinone derivatives.

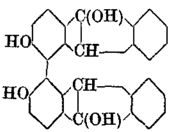
When the dihydroxyhelianthrone, preferably in the form of the acetyl derivative, is oxidised with chromic acid (Haller and Perkin, *loc. cit.*), the corresponding dihydroxy-1 : 1′-dianthraquinonyl is obtained. The positions of the hydroxyl groups in this compound have now been studied. Since no change occurred on fusion with alkali at 200—250°, it seemed unlikely that this could be the 2 : 7′- or 7 : 7′-dihydroxy-compound, because if this were so the formation of either a 2 : 7′ : 8′-trihydroxy- or 7 : 8 : 7′ : 8′-tetrahydroxy-derivative, the former containing one, and the latter two alizarin nuclei, was to be expected. 2 : 2′-Dihydroxy-1 : 1′-dianthraquinonyl (III) was therefore synthesised from 1-*bromo-2-benzoyloxyanthraquinone* (the 1-*chloro*-compound being much less satisfactory) by the Ullmann method (*Annalen*, 1904, **332**, 28) and subsequent hydrolysis, and proved to be identical in all respects with Haller and Perkin's substance. The helianthrone derived from 3-hydroxyanthranol is therefore the 2 : 2′-dihydroxy-derivative (IV).

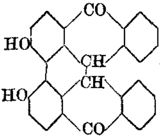
(III.)   (IV.)

1-*Bromo-2-hydroxyanthraquinone* can be obtained, in a similar manner to the 1-chloro-compound (Decker and Laube, *Ber.*, 1906, **39**, 112), from 2-hydroxyanthraquinone and hypobromite in theoretical amonnt. Excess of the reagent yields 1 : 3-*dibromo-2-hydroxyanthraquinone*, and from this, by mild fusion with 40% alkali in an autoclave, 3-bromoalizarin is obtained—a result indicating the more stable character of the β-halogen atom as compared with that in the α-position. 1 : 3-Dibromo-2-hydroxyanthraquinone has been described by Baeyer as the product of the action of sulphuric acid on tetrabromophenolphthalein (*Annalen*, 1880, **202**, 336); the melting points given for this compound, 207—208°, and its acetyl derivative, 189—190°, however, differ from those, 216—217° and 195°, recorded here. Baeyer, again, by the action of 50% alkali in an open dish at 200° for 3 hours, obtained, not 3-bromoalizarin, but alizarin itself. This further discrepancy is no doubt to be accounted for by the fact that during his experiment a considerable concentration of the alkali solution occurred.

Helianthrone can be prepared (Scholl, *Ber.*, 1910, **43**, 1734) from 1 : 1′-dianthraquinonyl by the action of aluminium and sulphuric acid—a reaction involving reduction and subsequent oxidation—

and 4 : 4′-dichlorohelianthrone has been obtained from the corresponding dichlorodianthraquinonyl in a similar manner (Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839). The conversion of (III) into (IV) was now studied, not only to complete the synthesis of the latter from 1-bromo-2-hydroxyanthraquinone, but with the special object of isolating one or other of the intermediate products of this reaction. This can hardly be accomplished by the aluminium-sulphuric acid method, and when stannous chloride and hydrochloric acid were employed, although indications of the presence of a substance of this character were obtained (Haller and Perkin, *loc. cit.*), its isolation was not found possible. By the action of zinc dust and ammonia on 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl (III) better results are obtained, for although a partial disruption of the dianthraquinonyl linkage is liable to occur, with eventual production of 3-hydroxyanthranol, the main product of the reaction is without doubt the *dihydroxydianthranolyl* (V).*

(V.) 

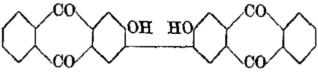
 (VI.)

This compound is extremely prone to oxidation, and by digestion with boiling nitrobenzene changes into 2 : 2′-dihydroxyhelianthrone (IV); on this account all attempts to prepare (VI) were unsuccessful.

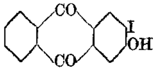
The fact that 2 : 2′-dihydroxyhelianthrone can be so easily iodinated in pyridine solution (*loc. cit.*) suggested that this method might be used in the case of other hydroxy-compounds, and an account of its application to certain hydroxyanthraquinones will be the subject of a later communication. 2-Hydroxyanthraquinone thus yielded a *monoiodo*-derivative, and as this substance appeared to be of interest in connexion with the present research, the orientation of the halogen atom was determined. Although alcoholic sodium methoxide (Decker and Laube, *loc. cit.*) converts 1-chloro-2-methoxyanthraquinone into a mixture of 1-hydroxy-2-methoxy- and 1 : 2-dimethoxy-anthraquinones, this iodo(methoxy)-compound merely suffered dehalogenation by such treatment, 2-methoxyanthraquinone being produced. Alkali fusion led to the formation of alizarin, suggesting the constitution 1-iodo-2-hydroxyanthraquinone; but this was not conclusive evidence, since 2 : 3-dibromo-

* For (V) without the 2- and 2′-hydroxyls the term *dianthranolyl*, and similarly for (VI) *dianthronyl*, is suggested.

anthraquinone gives a similar result (Battegay and Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632), 2 : 3-dihydroxyanthraquinone (hystazarin) being unstable in these circumstances. By the application, however, of the Ullmann method to the monoiodo-2-hydroxyanthraquinone, a dihydroxydianthraquinonyl was obtained which, being distinct from (III), can only be 3 : 3′-*dihydroxy*-2 : 2′-*dianthraquinonyl* (VII). Accordingly, when 2-hydroxyanthraquinone is treated with iodine in pyridine solution, the iodine enters the 3-position (VIII).



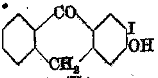
(VII.)



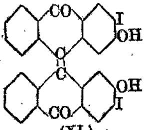
(VIII.)

The conversion of (VIII) into the 3 : 3′-di-iodo-2 : 2′-dihydroxyhelianthrone of Haller and Perkin (*loc. cit.*) was now attempted. Incidentally, the reduction of 1-chloro-2-hydroxyanthraquinone with ammonia and zinc dust, or with stannous chloride and boiling hydrochloric acid, was found to cause elimination of the halogen and formation of 3-hydroxyanthranol (identified as the acetyl derivative, m. p. 157—158°), but with aluminium and sulphuric acid a *chlorohydroxyanthranol* was produced. The orientation of the chloro- and hydroxy-groups present in this compound is under investigation.

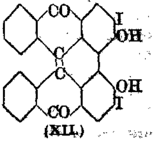
In a similar manner 3-*iodo*-2-*hydroxyanthraquinone* gave but one *anthranol* which experiment indicates has the constitution (X), the isomeric 3-iodo-2-hydroxy-compound being absent. On oxidation with ferric chloride, (X) yielded 2 : 2′-di-iodo-3 : 3′-dihydroxydianthrone, from which the *tetra-acetyl* derivative of *di-iododihydroxydianthranol* was prepared. This differed from the non-halogenated compound (Perkin and Yoda, *loc. cit.*) in that with iodine in pyridine solution the dianthraquinone (XI) was not obtained, and only by a treatment of the di-iododihydroxydianthranol itself with alkaline ferricyanide could this conversion be effected.



(X.)



(XI.)



(XII.)

Although 2 : 2′-di-iodo-3 : 3′-dihydroxydianthranol could be oxidised to the helianthrone by ferricyanide in excess, better results were

obtained with alkaline persulphate (compare Eckert and Tomaschek, *loc. cit.*). The 3 : 3′-di-iodo-2 : 2′-dihydroxyhelianthrone (XII) produced was identical with the iodination product of 2 : 2′-dihydroxyhelianthrone described above, and this, on further treatment with persulphate, yielded a compound which was not closely examined but was doubtless the corresponding naphthadianthrone.

Whereas 3 : 4-dihydroxyanthranol (deoxyalizarin) is readily oxidised to 3 : 4 : 3′ : 4′-tetrahydroxydianthrone, the conversion of the latter into the corresponding tetrahydroxydianthraquinone and tetrahydroxyhelianthrone could not be effected (Goodall and Perkin, J., 1924, **125**, 470). Owing to the presence of hydroxy-groups in the positions indicated, such compounds should be of tinctorial interest and attention was accordingly directed to 3 : 4 : 6-trihydroxyanthranol (deoxyanthrapurpurin; Cross and Perkin, J., 1927, 1297) in the hope that the 6-hydroxyl group of this substance, in that it may be considered analogous to that of 3-hydroxyanthranol itself, would favour these reactions. By using ferric chloride, the dianthrone can be obtained, but this is tedious to purify owing to the simultaneous production of an amorphous blue compound, and better results are obtained with hydrogen peroxide. The conversion of 3 : 4 : 6 : 3′ : 4′ : 6′-hexahydroxydianthrone into the corresponding dianthraquinone and helianthrone could not be effected owing, evidently, to its preferential oxidation to anthrapurpurin. Even by digestion with boiling acetone this colouring matter is produced, and all processes of mild oxidation give a similar result. It seems evident that other methods for the synthesis of dianthraquinones and helianthrones of this type must be discovered, and experiments in this direction are now in progress.

EXPERIMENTAL.

3 : 3′-*Di-iodo*-2 : 2′-*dihydroxyhelianthrone* (XII).—A solution of 2 : 2′-diacetoxyhelianthrone (1 g.) and iodine (3 g.) in pyridine (15 c.c.) was boiled for 10 minutes and poured into acidified sodium bisulphite solution. The maroon precipitate was again treated with iodine (3 g.) in pyridine (15 c.c.) as above. The yield was 1·288 g. (calc. for a di-iodo-compound, 1·33 g.). Acetylation in pyridine caused the rapid separation of 3 : 3′-*di-iodo*-2 : 2′-*diacetoxyhelianthrone* as small orange prisms, m. p. 268—270° (decomp.), after recrystallisation from much acetone; these dissolved in sulphuric acid with a green coloration, quickly changing to blue (Found: I, 32·8. $C_{32}H_{16}O_6I_2$ requires I, 33·6%). Hydrolysis with sulphuric acid in the presence of acetic acid gave the di-iododihydroxy-compound as minute maroon needles. When, however, the acetyl derivative in boiling pyridine was treated with a little diethylamine,

and the solution diluted with an equal bulk of acetic acid and treated with hydrochloric acid, the di-iododihydroxyhelianthrone was deposited in fair-sized leaflets having a beetle-green iridescence; these were sparingly soluble in the usual solvents and gave a blue solution in sulphuric acid. (The 3-iodo-2 : 2′-dihydroxyhelianthrone of Haller and Perkin, *loc. cit.*, can be crystallised in a similar manner.) With hydrosulphite and alkali a green vat is produced.

3 : 3′-*Dibromo*-2 : 2′-*dihydroxyhelianthrone*.—To 2 : 2′-diacetoxyhelianthrone (1 g.) in ice-cold pyridine (15 c.c.), bromine (1 g.) was slowly added. After 12 hours, the solution, when added to acidified sodium bisulphite, gave a brick-red precipitate (1·18 g. Calc. for a dibromo-derivative, 1·15 g.). 3 : 3′-Dibromo-2 : 2′-diacetoxyhelianthrone crystallises from acetic anhydride in orange-red prismatic needles, m. p. 293—296°, which dissolve in sulphuric acid with a pure blue coloration.

3-*Iodo*-2 : 2′-*diacetoxynaphthadianthrone*.—3-Iodo-2 : 2′-diacetoxyhelianthrone (1 g.) in benzene (1500 c.c.) was exposed to light for 3 weeks. Pale yellow, almost colourless needles separated, the fluorescence of the solution gradually disappearing. The product, m. p. above 340°, which gave a red solution in sulphuric acid and evolved iodine when strongly heated, without doubt had the above-stated constitution.

1 : 3-*Dibromo*-2-*hydroxyanthraquinone*.—To 2-hydroxyanthraquinone (2 g.) in boiling 1% sodium hydroxide solution (220 c.c.), sodium hypobromite (prepared from bromine, 4 g., and sodium hydroxide solution, 10 c.c.) was gradually added, and the digestion continued for 1 hour. The cold liquid, when poured into acidified sodium bisulphite solution, gave a precipitate which, after repeated crystallisation from alcohol, formed microscopic yellow needles, m. p. 216—217° (Found: C, 44·2; H, 1·7. $C_{14}H_6O_3Br_2$ requires C, 43·8; H, 1·8%).

1 : 3-*Dibromo*-2-*acetoxyanthraquinone* crystallises from acetic acid in yellow needles, m. p. 195° (Found: Br, 37·9. $C_{16}H_8O_4Br_2$ requires Br, 37·7%).

1 : 3-*Dibromo*-2-*methoxyanthraquinone*, prepared by means of methyl sulphate and alkali, separates from benzene in pale yellow, hair-like needles, m. p. 226—227° (Found: CH_3, 3·8. $C_{15}H_8O_3Br_2$ requires CH_3, 3·8%).

3-*Bromoalizarin*.—1 : 3-Dibromo-2-hydroxyanthraquinone (0·5 g.) was mixed with sodium hydroxide (7 g.) in water (10 c.c.) and heated in a small iron autoclave at 200° for 6 hours; the melt was then diluted with water, and the violet solution neutralised with acid. The dull yellow product was dried and extracted with boiling solvent naphtha, the extract agitated with dilute sodium hydroxide solu-

tion, and the alkaline liquid acidified. By acetylating the bright orange powder produced, an acetyl compound was obtained in needles, m. p. 201—202°. That this compound was diacetyl-3-bromoalizarin was evident from a mixed melting-point determination, the 3-bromoalizarin required for this purpose being prepared by the action of bromine on alizarin-3-sulphonic acid (Ger. Pat. 77179, 1905; Friedländer's "Fortschritte," IV, 330; compare Baeyer, *loc. cit.*).

1-*Bromo-2-acetoxyanthraquinone.*—To 2-hydroxyanthraquinone (1 g.) in 1% caustic soda solution (100 c.c.), bromine (0·7 g.) in 10% caustic soda solution (20 c.c.) was gradually added, and the liquid was slowly raised to its boiling point, allowed to cool, and neutralised with hydrochloric acid. The product (1·29 g.) was converted into the *acetyl* compound, which crystallised from acetone in yellow rods, m. p. 182—183° (Found: C, 55·4; H, 2·6; Br, 23·5. $C_{16}H_9O_4Br$ requires C, 55·6; H, 2·6; Br, 23·2%).

1-*Bromo-2-hydroxyanthraquinone*, obtained by the hydrolysis of the acetyl compound with hydrochloric acid in the usual manner, separated from alcohol in small yellow cubes, m. p. 185—187° (Found: C, 55·4; H, 2·3. $C_{14}H_7O_3Br$ requires C, 55·4; H, 2·3%).

1-*Bromo-2-methoxyanthraquinone*, obtained by the action of methyl sulphate and alkali, consisted of hair-like needles, m. p. 247° (Found: CH_3, 4·7. $C_{15}H_9O_3Br$ requires CH_3, 4·7%).

1-*Bromo-2-benzoyloxyanthraquinone.*—To 1-bromo-2-hydroxyanthraquinone (1 g.), suspended in chloroform (5 c.c.) and benzoyl chloride (2 c.c.), pyridine (1·5 c.c.) was added with good stirring. Reaction occurred without apparent solution, and after 24 hours the product was washed with alcohol (yield, 1·25 g.) and recrystallised from benzene, giving yellow needles, m. p. 229—230° (Found: C, 61·9; H, 2·75. $C_{21}H_{11}O_4Br$ requires C, 61·9; H, 2·7%).

2 : 2′-*Dihydroxy*-1 : 1′-*dianthraquinonyl* (III).—A solution of 1-bromo-2-benzoyloxyanthraquinone (0·3 g.) in naphthalene (0·8 g.) was boiled with copper powder (0·3 g.) for 2 hours. The product, freed from naphthalene by extraction with boiling alcohol, was digested with boiling 1% methyl-alcoholic potash and the crimson liquid was filtered, diluted with water, and acidified. The yellow deposit, acetylated with acetic anhydride and pyridine, yielded yellow plates which, after recrystallisation from acetic anhydride, melted at 278—279°, gave in sulphuric acid a scarlet solution slowly changing to black, and were identified, by a mixed melting-point determination, with the 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl which is obtained by the oxidation of 2 : 2′-diacetoxyhelianthrone with chromic acid in presence of acetic acid.

Attempts to prepare 2 : 2′-dibenzoyloxy-1 : 1′-dianthraquinonyl

as described above, but with tetralin instead of naphthalene as solvent, were unsuccessful because the tetralin caused elimination of the halogen; the sole product was 2-benzoyloxyanthraquinone.

1-Chloro-2-methoxyanthraquinone, prepared from the 1-chloro-2-hydroxy-compound, methyl sulphate, and alkali in the usual manner, separated from alcohol in yellow needles, m. p. 223—224°. After being heated (0·3 g.) with copper powder (0·3 g.) in boiling nitrobenzene (3 c.c.) for 2 hours, it was recovered unchanged.

1-*Chloro-2-benzoyloxyanthraquinone*.—To 1-chloro-2-hydroxy-anthraquinone (1·2 g.), suspended in a mixture of chloroform (6 c.c.) and benzoyl chloride (3 c.c.), pyridine (2 c.c.) was gradually added, and after 24 hours the product was collected, washed with alcohol (yield, 1·5 g.), and recrystallised from benzene, giving yellow needles, m. p. 228—230°. A mixture of this compound (0·4 g.), naphthalene (0·5 g.), and copper powder (0·3 g.) was boiled for 6 hours and the product was isolated and hydrolysed by the methods previously described. On acetylation, small plates of 2 : 2′-di-acetoxy-1 : 1′-dianthraquinonyl, m. p. 274°, were obtained in trifling amount.

2 : 2′-*Dihydroxy*-1 : 1′-*dianthranolyl* (V).—A solution of 2 : 2′-di-hydroxy-1 : 1′-dianthraquinonyl (1 g.) in concentrated ammonia (20 c.c.) and water (50 c.c.) was boiled, and zinc dust (3 g.) gradually added, access of air being prevented. After 15 minutes the greenish-yellow liquid was filtered into dilute hydrochloric acid and the pale yellow precipitate dried. Acetylation with acetic anhydride and pyridine gave a product which could be readily separated by extraction with boiling alcohol into two fractions, A remaining practically undissolved, and B passing into solution. From the extract, on cooling, B separated in colourless needles which, after removal in the same manner of a trace of A, melted at 157—158° and consisted, without doubt, of 3 : 9-*diacetoxyanthracene* (Found: C, 73·2; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%). A, recrystallised from alcohol–acetic acid, formed yellow prisms, m. p. 267—268°, which were somewhat sparingly soluble in sulphuric acid, giving a pale yellow solution (Found: C, 73·45; H, 4·5; $CH_3{\cdot}CO_2H$, 41·2. $C_{36}H_{26}O_8$ requires C, 73·7; H, 4·4; $CH_3{\cdot}CO_2H$, 40·9%).

This *tetra-acetyl* derivative of 2 : 2′-dihydroxy-1 : 1′-dianthranolyl was readily oxidised by chromic acid in the presence of acetic acid, yellow plates of 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl, m. p. 275—277°, being obtained. Hydrolysis with hydrochloric acid then gave 2 : 2′-*dihydroxy*-1 : 1′-*dianthranolyl* (V) as yellow cubes, which blackened at 270° and melted indefinitely at about 290° (Found: C, 80·2; H, 4·4. $C_{28}H_{18}O_4$ requires C, 80·3; H, 4·4%). It was almost insoluble in the usual solvents but gave yellow solutions in

alkalis. Boiling nitrobenzene dissolved it readily, but oxidation simultaneously occurred, a red powder separating. This with acetic anhydride and pyridine gave an acetyl compound in yellow needles, m. p. 277°, soluble in sulphuric acid with a violet coloration, which, as its properties and a mixed melting-point determination indicated, was 2 : 2′-diacetoxyhelianthrone.

Further experiments on the reduction of 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl with ammonia and zinc dust have shown that, if the latter is added all at once, the formation of 3-hydroxyanthranol can, with care, be avoided. By this method, 2 g. of the dianthraquinonyl gave 1·87 g. of dihydroxydianthranolyl (calc., 1·87 g.), from which a pure acetyl compound was at once obtained on acetylation in the usual manner. Boiling with stannous chloride and hydrochloric acid for 15 minutes gave dihydroxydianthranolyl mixed with some dihydroxyhelianthrone (and probably 3-hydroxyanthranol).

Chlorohydroxyanthranol.—To 1-chloro-2-hydroxyanthraquinone (3 g.) in sulphuric acid (60 c.c.) at 30—40°, aluminium powder (1 g.) was slowly added. After 1 hour, the yellow solution was poured into water (500 c.c.), the mixture slowly heated to boiling, and the precipitate collected (2·6 g.). Acetylation in pyridine gave *chlorodiacetoxyanthracene*, which crystallised from alcohol–acetic acid in light yellow cubes, m. p. 167—168° (Found : C, 65·7 ; H, 3·9 ; Cl, 10·9 ; $CH_3\cdot CO_2H$, 36·9. $C_{18}H_{13}O_4Cl$ requires C, 65·7 ; H, 3·95 ; Cl, 10·8 ; $CH_3\cdot CO_2H$, 36·5%). Hydrolysis with hydrochloric acid gave the *chlorohydroxyanthranol* as a greenish-yellow precipitate, which separated from acetic acid in prisms, m. p. 230° (Found : C, 68·7 ; H, 3·8. $C_{14}H_9O_2Cl$ requires C, 68·7 ; H, 3·7%).

3-Iodo-2-hydroxyanthraquinone.—Iodine (1·5 g.) was added to a solution of 2-hydroxyanthraquinone (0·6 g.) in pyridine (5 c.c.), and the mixture boiled for 15 minutes. On keeping, crystals separated which were collected (the mother-liquor being employed for a second operation) and washed with acidified sodium bisulphite solution (yield, 0·75 g.). The *acetyl* compound, obtained with acetic anhydride and pyridine, crystallised from acetic acid in large yellow needles, m. p. 224—225° (Found : C, 48·8 ; H, 2·4 ; I, 32·0. $C_{16}H_9O_4I$ requires C, 48·9 ; H, 2·3 ; I, 32·4%). On hydrolysis with hydrochloric acid it gave yellow needles of *3-iodo-2-hydroxyanthraquinone*, m. p. 278—279° after recrystallisation from alcohol, in almost theoretical yield (Found : C, 47·8 ; H, 2·1. $C_{14}H_7O_3I$ requires C, 48·0 ; H, 2·0%). This resembled 2-hydroxyanthraquinone in general properties and when fused with alkali at 200° yielded alizarin (identified as the acetyl compound).

3-Iodo-2-methoxyanthraquinone, prepared from the iodohydroxy-

compound, alkali, and methyl sulphate, separated from benzene in pale yellow needles, m. p. 228—229° (Found: C, 49·2; H, 2·3; CH_3, 4·2. $C_{15}H_9O_3I$ requires C, 49·4; H, 2·5; CH_3, 4·1%). Owing to the sparing solubility of this substance in hydriodic acid, two treatments with the latter were necessary to ensure complete demethylation.

With the object of substituting a methoxy-group for the iodine in 3-iodo-2-methoxyanthraquinone (compare Decker and Laube, *loc. cit.*) and thus ascertaining its exact position, 0·6 g. was heated with sodium methoxide (sodium, 3 g., in alcohol, 9 c.c.) at 110° in a sealed tube for 12 hours. The product was treated with water, and the undissolved residue crystallised from alcohol. The pale yellow needles obtained melted at 196°, and, as a mixed melting point showed, consisted of 2-methoxyanthraquinone.

3-*Amino-2-hydroxyanthraquinone* (?).—3-Iodo-2-hydroxyanthraquinone (1 g.) in concentrated ammonia (10 c.c.) and a trace of copper were heated at 160—180° in a small autoclave for 8 hours. The violet liquid was acidified, and the red precipitate crystallised by solution in much alcohol and concentration to a small bulk. The reddish-brown leaflets, which possessed a metallic iridescence, had no definite melting point (decomposing above 300°) and gave a yellow solution in sulphuric acid (Found: N, 5·9. $C_{14}H_9O_3N$ requires N, 5·85%). Attempts to prepare a dihydroxyanthraquinone from this compound by the diazotisation process (so as to establish the position of the iodo-group in the iodo-2-hydroxyanthraquinone) failed, and it is likely that the yellow product obtained by means of sodium nitrite and concentrated sulphuric acid is rather a diazo-oxide than a diazonium sulphate.

3-*Iodo-2-benzoyloxyanthraquinone*.—3-Iodo-2-hydroxyanthraquinone (1 g.) in chloroform (5 c.c.) and benzoyl chloride (2 c.c.) was treated with pyridine (1 c.c.). From the clear liquid on keeping, crystals separated, which, by recrystallisation from benzene, were obtained as yellow plates, m. p. 185° (Found: C, 55·3; H, 2·3. $C_{21}H_{11}O_4I$ requires C, 55·5; H, 2·4%).

3 : 3′-*Dihydroxy-2 : 2′-dianthraquinonyl* (VII).—A mixture of 3-iodo-2-benzoyloxyanthraquinone (1 g.), naphthalene (1·5 g.), and copper powder (0·5 g.) was boiled for 5 hours, and the product was worked up and finally acetylated as described on p. 186. The acetyl derivative obtained separated from benzene in colourless needles, m. p. 315° (Found: C, 72·15; H, 3·6. $C_{32}H_{18}O_8$ requires C, 72·45; H, 3·4%). This compound is therefore distinct from the 2 : 2′-diacetoxy-1 : 1′-dianthraquinonyl of Haller and Perkin (*loc. cit.*), which melts at 278—279°. The former, again, is soluble in sulphuric acid with an orange colour, whereas the latter thus yields

a crimson liquid which slowly changes to violet-black. The present compound is therefore 3 : 3′-*diacetoxy*-2 : 2′-*dianthraquinonyl.*

2-*Iodo*-3-*hydroxyanthranol* (X).—3-Iodo-2-acetoxyanthraquinone (5 g.) in sulphuric acid (130 c.c.) was gradually treated with aluminium powder (1·5 g.) at 35—40°. The pale yellow liquid was poured into water (1000 c.c.), and the mixture heated to boiling in order to granulate the precipitate (yield, 4·1 g.). Treatment with acetic anhydride and pyridine then gave the *diacetyl* compound, which crystallised from alcohol–acetic acid in colourless needles, m. p. 196° (Found: C, 51·5; H, 3·15; I, 30·6; CH_3·CO_2H, 29·2. $C_{18}H_{13}O_4I$ requires C, 51·4; H, 3·1; I, 30·6; CH_3·CO_2H, 28·6%). 2-*Iodo*-3-*hydroxyanthranol*, prepared by the hydrolysis of the acetyl compound with hydrochloric acid, crystallised from acetone in small plates, m. p. 239—240° (Found: C, 49·8; H, 2·8. $C_{14}H_9O_2I$ requires C, 50·0; H, 2·7%).

2 : 2′-*Di-iodo*-3 : 3′-*dihydroxydianthrone.*—To the diacetylanthranol (5·35 g.) in acetic acid (29 c.c.), ferric chloride (7·2 g.) in acetic acid (9·6 c.c.) was added, and the mixture was heated to boiling and then kept at 100° for 45 minutes. Yellow leaflets separated which, after cooling, were collected and washed with alcohol. The yield was 3·95 g. (74%; calc., 79·7%).

2 : 2′-*Di-iodo*-3 : 3′-*diacetoxydianthrone* can be prepared by the addition of a trace of sulphuric acid to a suspension of the dianthrone in acetic anhydride and boiling for a few seconds. It crystallises from acetic anhydride in plates, m. p. 227—228° after darkening at about 215°, which give a yellow solution in sulphuric acid (Found: C, 50·7; H, 3·0. $C_{32}H_{20}O_6I_2$ requires C, 50·9; H, 2·6%). With boiling acetic anhydride and pyridine, the *tetra-acetyl* derivative of 2 : 2′-di-iodo-3 : 3′-dihydroxydianthranol is produced, which separates from acetone in yellow prisms containing two molecules of acetone of crystallisation (Found: C, 53·0; H, 3·55. $C_{36}H_{24}O_8I_2$,$2C_3H_6O$ requires C, 42·8; H, 3·7%). When heated, it melts between 200° and 220°, resolidifies at about 260°, and melts again at 290°. Kept at 160° until constant in weight, it loses 12·1% of acetone (theory requires 12·2%) and then melts at 290°. Again, when alcohol is added to a solution of the tetra-acetyl derivative in acetic anhydride, the deposited crystals contain approximately one molecule of alcohol of crystallisation (Found: loss at 160°, 4·1. Theory requires loss, 5·2%). It separates, however, solvent-free from acetic anhydride and then melts at 293—295° (Found: C, 51·4; H, 3·0; CH_3·CO_2H, 29·1. $C_{36}H_{24}O_8I_2$ requires C, 51·55; H, 2·8; CH_3·CO_2H, 28·6%). Sulphuric acid dissolves it with a magenta coloration. Hydrolysis gave 2 : 2′-*di-iodo*-3 : 3′-*dihydroxydianthrone* as yellow needles which darkened at [illegible] and melted at [illegible] (Found:

C, 50·5; H, 2·5. $C_{28}H_{16}O_4I_2$ requires C, 50·15; H, 2·4%). The property of the tetra-acetyldi-iodoanthranol, which is apparently not possessed by the diacetyldianthrone, to separate from acetone with solvent of crystallisation which is retained with some tenacity is analogous to that of the unhalogenated tetra-acetyl compound (Perkin and Whattam, J., 1922, **121**, 293). The latter indeed it has now been found crystallises from benzene in brown prisms, $C_{36}H_{26}O_8,C_6H_6$, m. p. 175—177°, and from chloroform in prisms, probably $C_{36}H_{26}O_8,CHCl_3$, melting at 161° when quickly heated.

2 : 2'-*Di-iodo*-3 : 3'-*dihydroxydianthraquinone* (XI).—Attempts to prepare this compound by the action of iodine upon the tetra-acetyl-di-iododianthranol in pyridine solution having failed (compare Perkin and Yoda), 2 : 2'-di-iodo-3 : 3'-dihydroxydianthrone (2 g.) was dissolved in 10% sodium hydroxide solution (100 c.c.), the liquid well boiled, and, after cooling, 8% potassium ferricyanide solution (25 c.c.) slowly added. After 2 hours the suspension was neutralised by hydrochloric acid, the dull yellow precipitate collected (1·97 g.), and acetylated in pyridine. Without apparent solution, pale yellow plates, m. p. 306—308°, of 2 : 2'-di-iodo-3 : 3'-diacetoxydi-anthraquinone were obtained. These dissolved in sulphuric acid with a crimson colour passing to brown-black—a property of di-anthraquinone itself and its 3 : 3'-dihydroxy-compound (*loc. cit.*).

3 : 3'-*Di-iodo*-2 : 2'-*dihydroxyhelianthrone* (XII).—A solution of 2 : 2'-di-iodo-3 : 3'-dihydroxydianthrone (0·5 g.) in 5% sodium hydroxide solution (25 c.c.) was boiled and then filtered into a solution of potassium persulphate (1·5 g.) in water (50 c.c.), a brown deposit separating. The mixture was acidified and the crude helianthrone collected and dried (yield, 0·4 g.). The *diacetyl* compound, obtained in the usual manner and recrystallised from much acetone, consisted of orange prisms, m. p. 268—270°, which gave in sulphuric acid a green solution rapidly becoming blue (Found: C, 51·2; H, 2·9. $C_{32}H_{16}O_6I_2$ requires C, 51·2; H, 2·1%). A comparison of this compound with the acetylation product of the di-iododihydroxyhelianthrone obtained by the direct iodination of 2 : 2'-dihydroxyhelianthrone (*loc. cit.*) indicated that they were identical.

3 : 4 : 6 : 3' : 4' : 6'-*Hexahydroxydianthrone*.—To acetylanthra-purpurinanthranol (0·4 g.) in acetic acid (2 c.c.), ferric chloride (0·6 g.) in acetic acid (1 c.c.) was added and the mixture was boiled for 2 minutes and then kept at 100° for 1 hour. The green deposit (0·25 g.), which consisted of a yellow product mixed with a blue amorphous compound, was acetylated with acetic anhydride. The latter impurity, being unattacked, was removed by hot filtration,

and addition of alcohol to the filtrate caused the separation of 3 : 4 : 6 : 3′ : 4′ : 6′-*hexa-acetoxydianthrone* as colourless needles, m. p. 250—251° after recrystallisation from acetone (Found: C, 65·15; H, 4·2; $CH_3·CO_2H$, 50·1. $C_{40}H_{30}O_{14}$ requires C, 65·4; H, 4·1; $CH_3·CO_2H$, 49·0%).

The nature of the blue compound has not yet been ascertained. It is insoluble in the usual solvents, dissolves in sulphuric acid with a yellow coloration, and, as prepared above, contains iron, which is evidently in combination, as it is not removed by the action of boiling hydrochloric acid. Apparently the same substance, in this case iron-free, is in part produced when the hexa-acetyldianthrone is digested with boiling alcoholic sulphuric acid; this product will be further examined in due course. Snbsequent experiments have shown that by oxidising anthrapurpurinanthranol (5 g.) in alcohol (20 c.c.) and 10% caustic soda solution (10 c.c.) (boiling to effect solution and subsequently well cooling) with 100-volume hydrogen peroxide (10 c.c.), the dianthrone can be produced without admixture with this blue substance. After 5 hours the liquid was diluted with water and acidified with sulphuric acid and the dianthrone (4·8 g.) was washed with acetone and with ether. It was thus obtained as a pale green, amorphous powder which darkened at about 140° and blackened at 240°, but had no definite melting point. Although when acetylated it gives the crystalline acetyl compound referred to above, it has not itself been obtained in a crystalline condition, and indeed separates as a green powder when the acetyl compound is hydrolysed with hydrochloric acid in presence of acetic acid.

When 3 : 4 : 6 : 9-tetra-acetoxyanthracene (5 g.) in acetic acid (250 c.c.) was exposed to sunlight, colourless prisms slowly separated and the liquid, at first pale yellow, developed a green tint. After 5 weeks, the crystals (1·7 g.), which evidently consisted of 3 : 4 : 6 : 9 : 3′ : 4′ : 6′ : 9′-*octa-acetoxydianthranol*, were collected; after recrystallisation from acetic acid, they melted at 239—240° (Found: C, 64·7; H, 2·0. $C_{44}H_{34}O_{16}$ requires C, 64·6; H, 4·2%).

3 : 4 : 6 : 3′ : 4′ : 6′-Hexahydroxydianthrone is very susceptible to oxidation and its yellow solution in acetone, when boiled, gradually develops a red colour owing to the formation of anthrapurpurin, for the residue obtained on removal of the acetone gave on acetylation triacetylanthrapurpurin, m. p. 227°. Attempts to prepare the corresponding hexahydroxydianthraquinone and helianthrone from this dianthrone have failed, all gentle methods of oxidation giving anthrapurpurin. When the dianthrone (2 g.), suspended in ether (50 c.c.), was treated with diazomethane (nitrosomethylurethane, 8 c.c.), and the crude product crystallised from alcohol,

colourless needles of a methyl ether, m. p. 215—216°, were obtained. This compound has not yet been further investigated.

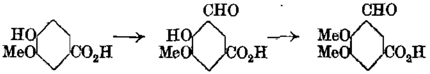
The authors are much indebted to the British Alizarine Co., Ltd., for the gift of some quantity of 2-aminoanthraquinone from which the 2-hydroxyanthraquinone employed in these experiments was prepared.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, November* 15*th*, 1928.]

XXVI.—*A Synthesis of* iso*Opianic Acid.*

By SATYENDRA NATH CHAKRAVARTI and WILLIAM HENRY PERKIN, jun.

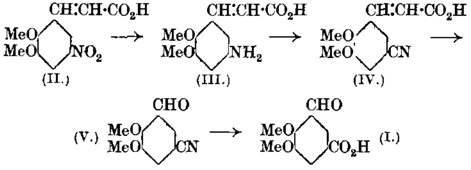
*iso*OPIANIC acid (I), m. p. 210—211°, was obtained in 1877 (*Ber.*, **10**, 397) by Tiemann and Mendelsohn by converting vanillic acid by boiling sodium hydroxide and chloroform into aldehydovanillic acid and methylating this with methyl iodide and potassium hydroxide.



(I.)

Since that date the acid does not appear to have been further investigated. During the course of experiments on the synthesis of the opianic acids we have carried out a synthesis of *iso*opianic acid which may be briefly described as follows. The starting point was 5-nitro-2 : 3-dimethoxycinnamic acid (II), which was obtained (i) by the nitration of 2 : 3-dimethoxycinnamic acid (Rubenstein, J., 1926, 651) and (ii) from 5-nitro-2 : 3-dimethoxybenzaldehyde (Davies, J., 1923, **123**, 1584; Perkin, Robinson, and Stoyle, J., 1924, **125**, 2357) by condensation with malonic acid in the presence of piperidine. The 5-nitro-acid was smoothly reduced by ferrous sulphate and ammonia to *5-amino-2 : 3-dimethoxycinnamic acid* (III) and this was then converted into the corresponding *5-cyano-2 : 3-dimethoxycinnamic acid* (IV) by the usual Sandmeyer process. The next step was the conversion of this acid into *5-cyano-2 : 3-dimethoxybenzaldehyde* (V), which was easily effected by oxidation with permanganate in the presence of benzene, and the cyanoaldehyde was readily hydrolysed on boiling with concentrated hydrochloric acid to *iso*opianic acid (I), which was identified with the acid described by Tiemann and Mendelsohn (*loc. cit.*) by the melting point, 210—211°, and by conversion into the methyl ester, m. p.

98—99°. The various steps in this synthesis may be formulated thus :



EXPERIMENTAL.

5-*Nitro*-2 : 3-*dimethoxycinnamic Acid* (II).—Most of the acid used in this investigation was made by the nitration of 2 : 3-dimethoxycinnamic acid, the separation from the small quantity of the 6-nitro-acid, produced at the same time, being carried out essentially in the manner recommended by Rubenstein (*loc. cit.*). The second method of preparation, which is at the same time additional proof of the constitution of the acid, was carried out as follows. 5-Nitro-2 : 3-dimethoxybenzaldehyde (10 g.), malonic acid (11 g.), and piperidine (0·5 c.c.) were heated in pyridine (25 c.c.) solution for 1½ hours on the steam-bath, rapid elimination of carbon dioxide taking place; the interaction was completed by boiling for 10 minutes. The product, when poured into excess of dilute hydrochloric acid, gave an almost quantitative yield of 5-nitro-2 : 3-dimethoxycinnamic acid; this, after being washed and dried, crystallised from glacial acetic acid in long colourless needles, m. p. 231° (Found : N, 5·6. Calc. for $C_{11}H_{11}O_6N$: N, 5·5%).

The methyl ester. The acid (1 g.), methyl alcohol (10 c.c.), and sulphuric acid (1 c.c.) were boiled under reflux for 4 hours. The methyl alcohol was boiled off, water added, and the *methyl* ester collected, washed with dilute sodium carbonate solution, and crystallised from alcohol, separating in needles, m. p. 154—155° (Found : N, 5·1. $C_{12}H_{13}O_6N$ requires N, 5·2%). The ethyl ester, prepared by passing hydrogen chloride into a suspension of the acid in alcohol, appears to be dimorphous, separating sometimes in thin plates and sometimes, especially from concentrated solution, in rosettes of needles, m. p. 116°.

5-*Amino*-2 : 3-*dimethoxycinnamic Acid* (III).—The 5-nitro-acid (10 g.), dissolved in dilute ammonia, was gradually added to a solution of freshly crystallised ferrous sulphate (80 g.) in water (160 c.c.) which had been heated to 90° on the steam-bath. Concentrated ammonia (32 c.c.) was then gradually added with shaking,

the mixture heated for ½ hour on the steam-bath, and the precipitate washed with a little dilute ammonia. The filtrate and washings were mixed with excess of hydrochloric acid and allowed to stand; the hydrochloride of 5-amino-2 : 3-dimethoxycinnamic acid which separated was recrystallised from dilute hydrochloric acid, separating in fine needles. The hydrochloride was dissolved in hot water and decomposed by adding a saturated solution of sodium acetate; the precipitated 5-*amino*-2 : 3-*dimethoxycinnamic acid* separated from alcohol in glistening prismatic plates, m. p. 233° (decomp.) (Found : N, 6·4. $C_{11}H_{13}O_4N$ requires N, 6·3%).

5-*Cyano*-2 : 3-*dimethoxycinnamic Acid* (IV).—5-Amino-2 : 3-dimethoxycinnamic acid (4·4 g.), water (22 c.c.), and concentrated hydrochloric acid (4·6 c.c.) were mixed at 0° with a solution of sodium nitrite (1·5 g. in 10 c.c. of water) and the diazo-solution, filtered from a trace of insoluble matter, was added to a hot solution of potassium cupro-cyanide obtained by adding potassium cyanide (5·6 g. in 10 c.c. of water) to a solution of copper sulphate (5 g. in 30 c.c. of water). The mixture was heated for ½ hour on the steam-bath, cooled, and acidified with concentrated hydrochloric acid, the precipitate was collected, washed, and dissolved in cold aqueous sodium carbonate, and this solution was filtered and acidified with hydrochloric acid. The precipitated *cyano-acid* crystallised from alcohol, with the aid of norite, in needles, m. p. 251° (Found : C, 61·5; H, 4·9. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7%). It is almost insoluble in cold water, sparingly soluble in ether or benzene, and readily soluble in boiling alcohol.

5-*Cyano*-2 : 3-*dimethoxybenzaldehyde* (V).—The cyano-acid (1 g.), dissolved in sodium carbonate solution, was covered with benzene (100 c.c.) in a separating funnel and a cold saturated solution of permanganate (1·4 g.) was gradually added with vigorous shaking. The liquids were filtered, the benzene layer was separated and dried over anhydrous sodium sulphate, and most of the benzene was distilled off; the *cyano-aldehyde* (0·6 g.) slowly separated in needles and, after recrystallisation from benzene, melted at 135° (Found : C, 63·1; H, 4·8. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7%).

iso*Opianic Acid* (I).—5-Cyano-2 : 3-dimethoxybenzaldehyde (0·5 g.) was heated on the steam-bath with concentrated hydrochloric acid (15 c.c.) for 3 hours; on cooling, almost pure *iso*opianic acid crystallised. It was collected, dissolved in cold dilute sodium carbonate solution, filtered, reprecipitated, and crystallised from water, separating in slender needles, m. p. 210—211° (Found : C, 57·0; H, 4·7. Calc. for $C_{10}H_{10}O_5$: C, 57·1; H, 4·8%). The methyl ester was prepared direct from 5-cyano-2 : 3-dimethoxybenzaldehyde by boiling with methyl alcohol and concentrated

sulphuric acid under reflux for 4 hours. The product was diluted with water and extracted with ether, the ethereal solution washed with dilute aqueous sodium carbonate and dried over anhydrous sodium sulphate, the ether evaporated, and the residue crystallised from water, from which it separated in needles, m. p. 98—99° as stated by Tiemann and Mendelsohn (*loc. cit.*).

THE DYSON PERRINS LABORATORY,
OXFORD.

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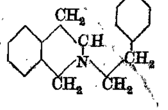
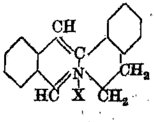
XXVII.—*Synthesis of* 3 : 10-*Dimethoxytetrahydroprotoberberine.*

By SATYENDRA NATH CHAKRAVARTI and WILLIAM HENRY PERKIN, jun.

ATTENTION has been directed (J., 1927, 2267, 2275) to the interest attaching to the synthesis of alkaloids which, although built up on the palmatine–berberine skeleton, do not contain the pyrocatechol nuclei so widely met with in the substances of this group which occur in nature. With the object of synthesising such substances and also of determining their ease of formation and of comparing their properties and the properties of their salts with those of the naturally occurring alkaloids, two series of experiments were undertaken. In the first place, the synthesis of the parent substance of this group, tetrahydroprotoberberine (I), was successfully carried out and it was shown (i) that this substance is much more difficult to synthesise than the derivatives, such as tetrahydroberberine, which contain two pyrocatechol nuclei, and (ii) that the protoberberinium salts (II) derived from it by oxidation differ in many ways from the corresponding berberinium salts; for example, instead of being bright orange or orange-yellow, they are only very slightly coloured.

(I.)

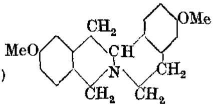
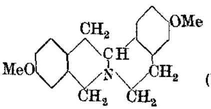




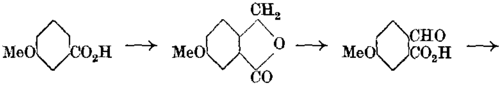
(II.)

The second series of experiments was concerned with the synthesis of alkaloids of an intermediate type containing, in the place of the two pyrocatechol nuclei, two benzene rings each containing one methoxy-group. The two substances selected for synthesis were

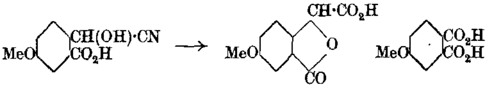
3 : 11-dimethoxytetrahydroprotoberberine (III) and 3 : 10-dimethoxytetrahydroprotoberberine (IV).*

(III.)   (IV.)

The synthesis and properties of the substance (III) have already been described (*loc. cit.*, p. 2267) and the present communication deals with the synthesis and properties of the isomeride (IV). After several attempts to effect the synthesis on lines similar to those laid down in the case of the alkaloid (III) had proved unavailing, the desired result was achieved by making use of a scheme of synthesis based on the conversion of meconinecarboxylic acid into oxyberberine by Perkin, Rây, and Robinson (J., 1925, **127**, 740). In employing this method, it was necessary in the first place to prepare 4-methoxyphthalidecarboxylic acid (VIII), and this we thought might be obtained by making use of the following series of changes:



(V.) (VI.) (VII.)



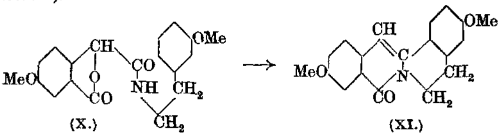
(VIII.) (IX.)

m-Methoxybenzoic acid (V) readily condenses with formaldehyde in the presence of hydrochloric acid under the conditions described by Edwards, Perkin, and Stoyle (J., 1925, **127**, 197), giving a good yield of 4-methoxyphthalide (VI), and the attempt was made to oxidise this with manganese dioxide and sulphuric acid to 4-methoxyphthalaldehydic acid (VII) under the conditions which so readily convert meconine into opianic acid. Unfortunately the oxidation could not be arrested at this stage, the main product being always 4-methoxyphthalic acid (IX) and therefore the scheme had to be abandoned. This easy method of preparation of 4-methoxyphthalic acid is, however, of interest, because this acid has been obtained as a degradation product both of thebaol (Pschorr, Seydel, and Stöhrer, *Ber.*, 1902,

* The nomenclature and numbering are discussed in J., 1925, 127, 1462.

35, 4401) and of colchicine (Windaus and Schiele, *Nachr. Ges. Wiss. Göttingen*, 1923, 17). We ultimately succeeded in preparing 4-methoxyphthalidecarboxylic acid (VIII) by acting on methyl 4-methoxybenzoate with chloral hydrate and sulphuric acid under the conditions recommended by Fritsch (*Annalen*, 1897, **296**, 351) for the preparation of substituted trichloromethylphthalides. The 4-methoxytrichloromethylphthalide, $MeO{\cdot}C_6H_3{<}^{CH(CCl_3){\cdot}O}_{CO}$, obtained in this way yielded 4-methoxyphthalidecarboxylic acid on hydrolysis with sodium hydroxide.

The acid chloride, obtained on treatment with thionyl chloride, condensed readily in benzene solution with β-*m*-methoxyphenylethylamine (Helfer, *Helv. Chim. Acta*, 1924, 7, 945), yielding *4-methoxyphthalidecarboxy-*β-m-*methoxyphenylethylamide* (X). When this was heated with phosphorus oxychloride, and the product decomposed with ice, a basic substance separated which, on reduction with zinc dust and acetic acid, was converted into a colourless substance, m. p. 180°, having all the properties of a compound of the oxyberberine type and this is doubtless 3 : 10-*dimethoxyoxyprotoberberine* (XI) (compare Perkin, Rây, and Robinson, *loc. cit.*).



(X.) (XI.)

When this substance was reduced electrolytically, it yielded a colourless crystalline tetrahydro-alkaloid, m. p. 139°, which is doubtless 3 : 10-*dimethoxytetrahydroprotoberberine* (IV), and in all its properties this isomeride shows the closest resemblance to the 3 : 11-dimethoxytetrahydroprotoberberine (III), m. p. 111°, obtained in the manner described in the earlier communication (*J.*, 1927, 2267).

The points of general interest emphasised in connexion with the synthesis and properties of the 3 : 11-isomeride (*loc. cit.*, p. 2269) are equally applicable to the present case and need not be repeated.

EXPERIMENTAL.

m-Methoxybenzoic acid may be obtained in a yield of 90% by the following method: *m*-Methoxybenzaldehyde (10 g.) (Chakravarti, Haworth, and Perkin, *J.*, 1927, 2269) is oxidised, in hot acetone solution, with 10% aqueous permanganate (120 c.c.),

sufficient acetone being added from time to time to keep the aldehyde in solution. After the manganese precipitate has been filtered off and washed, the alkaline solution is distilled to remove acetone, filtered, and acidified; a voluminous precipitate of almost pure *m*-methoxybenzoic acid then separates which may be obtained in colourless needles, m. p. 109—110°, by crystallisation from water.

Methyl *m*-methoxybenzoate is readily prepared by saturating a solution of the acid (10 g.) in methyl alcohol (50 c.c.) with hydrogen chloride and refluxing for 4 hours. Water is added, the oil extracted with ether, the ethereal solution well washed with dilute aqueous sodium carbonate and dried over sodium sulphate, and the ether removed; when the residue is distilled under 10 mm. the methyl ester passes over at 121—124°.

4-*Methoxyphthalide* (VI).—(i) *m*-Methoxybenzoic acid (2 g.), formaldehyde solution (6 c.c. of 40%), and concentrated hydrochloric acid (10 c.c.) were heated together on the steam-bath for 1 hour. The product was diluted with water and cooled; 4-methoxyphthalide containing some unchanged acid then separated. The solid was shaken with dilute sodium carbonate solution, and the undissolved part crystallised from methyl alcohol and then from water, from which the substance separated in long needles, m. p. 120°, identical with the 4-methoxyphthalide obtained by Fritsch (*loc. cit.*) (Found: C, 65·8; H, 4·9. Calc. for $C_9H_8O_3$: C, 65·8; H, 4·9%).

(ii) A slightly improved yield was obtained when *m*-methoxybenzoic acid (3 g.), dissolved in hot glacial acetic acid (10 c.c.), was mixed with concentrated hydrochloric acid (15 c.c.) and formaldehyde (6 c.c. of 40%) and boiled for an hour. Excess of sodium carbonate was added, the whole shaken with chloroform, the extract dried over potassium carbonate, the solvent removed, and the 4-methoxyphthalide recrystallised as before.

4-*Methoxyphthalic Acid* (IX).—The phthalide (2 g.), dissolved in warm sodium hydroxide solution (100 c.c. of 5%), was oxidised in the cold by the gradual addition of permanganate solution (3 g. in 100 c.c. of water). After 24 hours, the mixture was warmed for a few minutes on the steam-bath, sulphur dioxide passed in, hydrochloric acid added, and the whole concentrated to a small bulk and left in the ice-chest; 4-methoxyphthalic acid then separated in needles. The acid crystallised from water, in which it is readily soluble, in needles, melting at 168—170° with loss of water and formation of the anhydride, m. p. 95° (Found: C, 55·0; H, 4·1. Calc. for $C_9H_8O_5$: C, 55·1; H, 4·1%).

4-*Methoxyphthalidecarboxylic Acid* (VIII).—This acid was prepared by the following modification of Fritsch's method (*loc. cit.*,

p. 355). A mixture of methyl *m*-methoxybenzoate (10 g.), chloral hydrate (10 g.), and sulphuric acid (100 g.) was left for 5 days, being shaken from time to time. The product was poured on ice, and the precipitate was collected, washed, and crystallised from alcohol, a nearly quantitative yield of 4-methoxytrichloromethylphthalide, m. p. 135°, being obtained. This substance was warmed with an equal weight of sodium hydroxide in water (6 parts) until solution was complete. After being extracted with ether, the alkaline solution was acidified with concentrated hydrochloric acid and left for several hours; almost pure 4-methoxyphthalidecarboxylic acid then separated: after recrystallisation from benzene, it had m. p. 170°.

4-*Methoxyphthalidecarboxy*-β-m-*methoxyphenylethylamide* (X).—4-Methoxyphthalidecarboxylic acid (5 g.) and thionyl chloride (20 c.c.) were gently boiled for 2 hours in a reflux apparatus fitted with a calcium chloride tube. The excess of thionyl chloride was completely removed by distillation below 100° in a vacuum, and the acid chloride was dissolved in benzene (50 c.c.) and gradually added to a benzene solution of β-*m*-methoxyphenylethylamine (prepared from 5·5 g. of the hydrochloride). After 12 hours, the mixture was boiled under reflux for 2 hours, concentrated, and left in the ice-chest; most of the *amide* then crystallised. It was ground with very dilute sodium carbonate solution, collected, and recrystallised from alcohol, separating in rosettes of needles (8 g.), m. p. 129° (Found: C, 66·6; N, 5·5. $C_{19}H_{19}O_5N$ requires C, 66·9; H, 5·5%).

3 : 10-*Dimethoxyoxyprotoberberine* (XI).—The above amide (5 g.) and freshly distilled phosphorus oxychloride (50 c.c.) were heated together in a reflux apparatus, fitted with a calcium chloride tube, on the steam-bath for 6 hours. The product was decomposed by the careful addition of crushed ice, the liquid filtered, and the bright yellow filtrate rendered faintly alkaline with dilute sodium hydroxide solution. The ochre-coloured base which was precipitated was collected, washed with water, and dried in the air on porous porcelain. As the attempt to recrystallise the substance was unsuccessful, the whole was mixed with glacial acetic acid (125 c.c.), zinc dust (25 g.), and a few small crystals of copper sulphate and boiled for 5 minutes; a second similar portion of zinc dust was then added and the boiling continued for ½ hour. The cold product was diluted with a large volume of ethyl acetate, the solution washed several times with dilute hydrochloric acid, then with aqueous sodium hydroxide and with water, dried over potassium carbonate, and filtered, and the solvent removed by distillation. The pale yellow, crystalline residue was recrystallised several times from alcohol and obtained as a mass of almost colourless needles (3 g.),

m. p. 180° (Found: C, 74·5; H, 5·4; N, 4·7. $C_{19}H_{17}O_3N$ requires C, 74·3; H, 5·5; N, 4·6%).

3 : 10-*Dimethoxyoxyprotoberberine* dissolves to a faint violet solution in concentrated sulphuric acid, and the addition of a drop of concentrated nitric acid develops first a green and then a deep bluish-violet coloration which finally changes to a fine orange-red: on dilution with water the colour is discharged.

3 : 10-*Dimethoxytetrahydroprotoberberine* (IV).—3 : 10-Dimethoxyoxyprotoberberine (1 g.), dissolved in a mixture of alcohol (60 c.c.) and concentrated sulphuric acid (30 c.c.), was reduced in an electrolytic cell by a current of 6 amps. for 24 hours, the temperature being kept below 30°. The colourless solution was diluted with water and filtered, and the filtrate made strongly alkaline with sodium hydroxide and extracted with chloroform. The extract was dried over potassium carbonate, the solvent removed, and the solid residue converted into the sparingly soluble hydrochloride by the addition of dilute hydrochloric acid. This was recrystallised from water with the aid of norite, and the pure hydrochloride was dissolved in water and mixed with sodium hydroxide. The nearly pure 3 : 10-*dimethoxytetrahydroprotoberberine* separated from methyl alcohol in colourless prisms, m. p. 139° (Found: C, 77·5; H, 7·1. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1%).

One of us (S. N. C.) desires to thank the United Provinces Government for a scholarship which has enabled him to take part in these researches.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, December 4th*, 1928.]

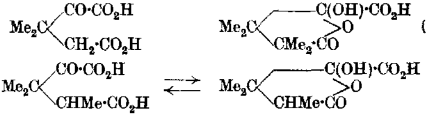
XXVIII.—*Studies in Keto-lactol Tautomerism. Part I. Ring-chain Tautomerism in α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid and a Synthesis of γ-Acetyl-ββ-dimethylbutyric Acid.*

By MUHAMMAD QUDRAT-I-KHUDA.

RING-CHAIN tautomerism has been divided by Kon, Stevenson, and Thorpe (J., 1922, **121**, 651) into two types, namely, keto-cyclol tautomerism, which has been exhaustively investigated by Thorpe and his collaborators (Deshapande and Thorpe, J., 1922, **121**, 1432; Singh and Thorpe, J., 1923, **123**, 114; Bains and Thorpe, *ibid.*, p. 1207; Lanfear and Thorpe, *ibid.*, pp. 1685, 2868), and keto-lactol tautomerism, as an example of which γ-keto-αββ-trimethyl-

glutaric acid (Balbiano's acid) may be cited : this reacts in both the keto-form (II) and the hydroxy-ring form (III) (Kon, Stevenson, and Thorpe, *loc. cit.*); its lower homologue exists in the keto-form (I) (Perkin and Thorpe, J., 1901, **79**, 757), and the next higher homologue only in the hydroxy-ring form (IV) (Rothstein and Shoppee, J., 1927, 532).

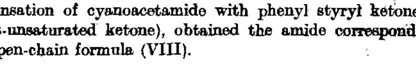
(I.) (IV.) (II.) (III.)



In the present series of papers, evidence will be brought forward of the existence of the latter type of tautomerism in some δ-ketonic acids. The effect of alteration of the carbon tetrahedral angle, due to the presence of different substituents, on the tautomeric character of the various acids will also be examined.

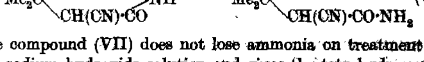
α-Carboxy-γ-acetyl-ββ-dimethylbutyric acid has been prepared by the alkaline hydrolysis of the condensation product of cyanoacetamide and mesityl oxide (compare Vorländer and Gärtner, *Annalen*, 1898, **304**, 17). Its reactions cannot be fully explained by the keto-formula (V) and it is necessary to assume that under certain conditions the acid exists in its lactol modification (VI).

(V.) (VI.)



When mesityl oxide is condensed with cyanoacetamide in the presence of a small quantity of sodium ethoxide, 6-*hydroxy*-2-*keto*-3-*cyano*-4 : 4 : 6-*trimethylpiperidine* (VII) is formed. Kohler and Souther, however (*J. Amer. Chem. Soc.*, 1922, **44**, 2906), by the condensation of cyanoacetamide with phenyl styryl ketone (also an αβ-unsaturated ketone), obtained the amide corresponding to the open-chain formula (VIII).

(VII.) (VIII.)



The compound (VII) does not lose ammonia on treatment with dilute sodium hydroxide solution and gives the tetrahydropyridine *derivative*, $Me_2C<{CH_2—CMe \atop CH(CN)·CO}>N$ (IX), on dehydration with phosphorus oxychloride. The constitution thus indicated is confirmed by the synthesis of the compound from the open-chain *cyano-ester* (X) : this, on treatment with ammonia, gives a crystalline com-

pound (XI) which, on being heated with alcoholic sodium ethoxide, is quantitatively converted into the compound (VII).

$$\text{(X.)}\quad Me_2C\begin{cases}CH_2\cdot COMe\\ CH(CN)\cdot CO_2Et\end{cases}\qquad Me_2C\begin{cases}CH_2\cdot CMe(OH)\cdot NH_2\\ CH(CN)\cdot CO\cdot NH_2\end{cases}\quad\text{(XI.)}$$

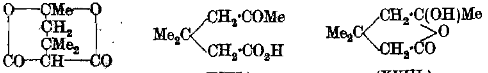
The compound (VII), when hydrolysed with concentrated aqueous potash, gives as the sole product the acid (V), the ethyl ester (XII) of which, on treatment with alcoholic sodium ethoxide, changes almost quantitatively into ethyl 5 : 5-dimethyl-5 : 6-dihydroresorcinol-4-carboxylate (XIII) (Vorländer, *Annalen*, 1897, **294**, 300).

$$\text{(XII.)}\quad Me_2C\begin{cases}CH_2\cdot CO\cdot CH_3\\ CH(CO_2Et)_2\end{cases}\qquad Me_2C\begin{cases}CH_2\text{———}CO\\ CH(CO_2Et)\cdot CO\end{cases}\!\!>CH_2\quad\text{(XIII.)}$$

The acid (V) on oxidation with sodium hypobromite solution gives α-carboxy-ββ-dimethylglutaric acid, $CO_2H\cdot CH_2\cdot CMe_2\cdot CH(CO_2H)_2$ (XIV) (Perkin and Goodwin, J., 1896, **69**, 1473), which changes into ββ-dimethylglutaric acid, $CMe_2(CH_2\cdot CO_2H)_2$ (XV), on heating.

Hydrolysis of (VII) with concentrated hydrochloric acid yields as the principal product a neutral crystalline solid, m. p. 137°, which gives the acid (V) when heated with dilute sodium hydroxide solution and is therefore probably the dilactone (XVI) (Vorländer and Gärtner, *Annalen*, 1898, **304**, 16); it is produced from the acid (V) almost quantitatively by heating with concentrated hydrochloric acid and quantitatively by the action of any dehydrating agent.

The acid (V) decomposes at 130—140°, giving a mixture containing the keto-monobasic acid (XVII) and the dilactone (XVI) in relative quantities which suggest that the parent acid is a mixture of the forms (V) and (VI), the generators of (XVII) and (XVI) respectively, approximately in the ratio 3 : 1.



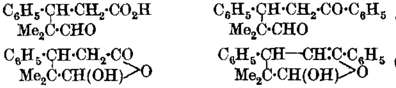
(XVI.) (XVII.) (XVIII.)

The proof of the existence of the hydroxyl group in the lactol form (VI) of the acid (V) is difficult to obtain. The ease with which lactonisation takes place precludes the formation of the acetyl derivative. It seemed probable that the desired evidence might be obtained if the possibility of dilactone formation were prevented, and therefore the keto-monobasic acid (XVII; lactol form, XVIII) was investigated.

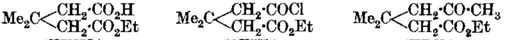
Meerwein and his collaborators have observed (*J. pr. Chem.*, 1927, 116, 536) that β-phenyl-γγ-dimethylglutaraldehydic acid (XIX) and

the δ-keto-aldehyde (XX) sometimes react as their lactol forms (XXI) and (XXII) respectively. It was expected that the acid (XVII) would exhibit similar properties. The acid was prepared, as already

(XIX.) (XX.) (XXI.) (XXII.)



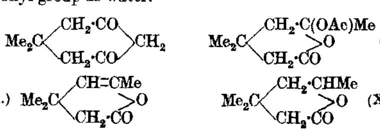
mentioned, from the acid (V). It had previously been obtained by Bredt (*Annalen*, 1898, **299**, 177) and by Vorländer and Gärtner (*loc. cit.*). Its constitution was further proved by an independent synthesis of its ethyl ester (XXV) from *ethyl hydrogen* ββ-*dimethylglutarate* (XXIII), through the acid chloride (XXIV) with zinc methyl iodide. The ester was completely converted into Vorländer's



(XXIII.) (XXIV.) (XXV.)

dimethyldihydroresorcinol (XXVI) (*Annalen*, 1897, **294**, 314) by alcoholic sodium ethoxide. The acid (XVII), on esterification with alcohol and mineral acid, gave the normal ester (XXV). The identity of the two esters was established by analysis and by the melting point of a mixture of their semicarbazones. The free acid was prepared from the synthetic ester and identified, by means of the semicarbazones, with the acid obtained from (X). Although the free acid appears to have the normal ketonic structure (XVII), it reacts in the isomeric hydroxy-form (XVIII) in presence of acetyl chloride, when, instead of the acetyl compound (XXVII), the unsaturated lactone (XXVIII) is obtained through elimination of the hydroxyl group as water.

(XXVI.) (XXVII.) (XXVIII.) (XXIX.)



The unsaturated lactone can be hydrolysed to the keto-acid (XVII) with alcoholic caustic potash. The keto-acid (XVII) on reduction with sodium and alcohol gives a good yield of the saturated *lactone* (XXIX). A study of the action of potassium cyanide on these lactones and of the synthesis of trisubstituted adipic acids is now in progress.

The proximity of a methylene-group to the keto-group in the acid (XVII) makes the elimination of a molecule of water an easy matter,

and consequently the unsaturated lactone (XXVIII) is readily obtained. But if the γ-carbon atom were substituted, more definite evidence of the existence of the hydroxy-phase of these keto-acids should be obtained. Experiments in this direction are in progress and the δ-keto-acid derived from the acid ester of camphoric acid does actually show interesting properties; the results, however, will form the subject of a future communication.

Experimental.

6-*Hydroxy*-2-*keto*-3-*cyano*-4 : 4 : 6-*trimethylpiperidine* (VII).—When a solution of sodium (2·3 g.) in absolute alcohol (500 c.c.) is mixed with powdered cyanoacetamide (84 g.) and mesityl oxide (108 c.c.) and well shaken, after 10—15 minutes crystals begin to separate and the alcohol sometimes boils. After 12 hours, the crystals are collected and washed with absolute alcohol; the mother-liquor and washings, when neutralised with hydrochloric acid and concentrated, give a few grams more of the same product (total yield, almost theoretical). The solid, after crystallising from ethyl alcohol and drying in the steam-oven, melts at 272° with charring (Found: C, 59·4; H, 7·5. $C_9H_{14}O_2N_2$ requires C, 59·3; H, 7·7%). It is somewhat soluble in water, soluble in hot alcohol, and insoluble in ether, benzene and chloroform. Sodium nitrite in cold acetic acid solution has no action on it.

2-*Keto*-3-*cyano*-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine* (IX).—The preceding compound (18 g.) is heated with phosphorus oxychloride (15 c.c.) on the steam-bath for 2 hours and the viscous mass obtained on cooling is treated with ice and a slight excess of dilute sodium carbonate solution. The precipitate obtained, after being washed with water and dried (9 g.), crystallises from hot dilute acetic acid in slender short needles, m. p. 253° (Found: C, 65·3; H, 7·1. $C_9H_{12}ON_2$ requires C, 65·8; H, 7·3%), which are very soluble in alcohol, appreciably soluble in dilute mineral acids, but insoluble in ether, chloroform and benzene.

Ethyl α-Cyano-γ-acetyl-ββ-dimethylbutyrate (X).—A solution of sodium (1·2 g.) in absolute alcohol (150 c.c.) is mixed with ethyl cyanoacetate (56 g.) and mesityl oxide (54 c.c.) and heated on the steam-bath for 4 hours; the alcohol is then distilled off and the residue poured into water. Ether extracts a liquid which, when washed, dried, and fractionated in a vacuum, gives first unchanged mesityl oxide and ethyl cyanoacetate and then the *ketocyano-ester* (X) as a colourless mobile liquid, b. p. 160°/16 mm., $d_4^{20\cdot3^\circ}$ 1·03705, $n_D^{20\cdot3^\circ}$ 1·44652, whence $[R_L]_D$ 54·39 (calc., 54·43) (Found: C, 62·0; H, 8·0. $C_{11}H_{17}O_3N$ requires C, 62·5; H, 8·0%). The yield is about 70%. The *semicarbazone*, crystallised from dilute methyl alcohol,

melts at 166·5° (Found: C, 53·8; H, 7·8. $C_{12}H_{20}O_3N_4$ requires C, 53·7; H, 7·5%).

Action of Aqueous Ammonia on Ethyl α-Cyano-γ-acetyl-ββ-dimethylbutyrate.—When the ester (25 g.) is mixed with aqueous ammonia (24 c.c., *d* 0·880) and occasionally shaken, the separate layers disappear after 24 hours, and after another 24 hours crystals begin to form. Next day, the whole is cooled in a freezing mixture and diluted with acetone and the crystals are collected and dried in the air. On recrystallisation from water, *δ-amino-δ-hydroxy-α-cyano-ββ-dimethylhexoamide* (XI) is obtained in crystals containing $3H_2O$, m. p. 87° (decomp.) (Found: C, 42·7; H, 9·1. $C_9H_{17}O_2N_3,3H_2O$ requires C, 42·7; H, 9·1%). It is soluble in water and in alcohol, but crystallises from the former only when the solution is cooled in ice. It is very sparingly soluble in hot chloroform and acetone and insoluble in ether and benzene. When left in a vacuum desiccator, it loses a part of its water and is converted into a sticky mass. It decomposes in the steam-oven, and loses ammonia when heated with water at 100°. It does not give a semicarbazone.

Hydrolysis of the Condensation Product (VII) *with Concentrated Hydrochloric Acid. Formation of the Dilactone* (XVI).—The powdered condensation product (20 g.) is heated with 100 c.c. of concentrated hydrochloric acid on the steam-bath for 4 hours, and the crystalline product is separated from the cooled, diluted solution and washed with and recrystallised from dilute alcohol, the *dilactone* being obtained in long prismatic needles, m. p. 137° (Found: C, 58·7; H, 6·8. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%), sparingly soluble in cold alcohol, difficultly soluble in ether and hot benzene, and freely soluble in hot alcohol. At 200°, it slowly decomposes with loss of carbon dioxide and production of the unsaturated lactone (XXVIII). The dilactone is also produced by hydrolysis of (IX) or (X) with concentrated hydrochloric acid.

Hydrolysis of the Condensation Product (VII) *with Concentrated Potassium Hydroxide Solution. Formation of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid* (V).—The compound (VII) (36 g.) is heated with a solution of potassium hydroxide (32 g.) in 130 c.c. of water until ammonia ceases to be evolved (about 28 hours). The cooled, diluted solution is acidified with concentrated hydrochloric acid, with cooling, and saturated with ammonium sulphate. Ether then extracts the acid (V), which crystallises from chloroform–petrol in stout prisms, m. p. 95° (Found: C, 53·4; H, 7·0. Calc. for $C_9H_{14}O_5$: C, 53·4; H, 6·9%. Found: Ag, 51·8. Calc. for $C_9H_{12}O_5Ag_2$: Ag, 51·9%).

The semicarbazone of (V) crystallises from a small quantity of

water in short prisms, m. p. 177° (Found: C, 46·3; H, 6·8. Calc.: C, 46·3; H, 6·6%). The ethyl ester (XII), prepared by means of alcoholic hydrogen chloride, has b. p. 153°/12 mm., $d_{4°}^{20·2°}$ 1·03921, $n_{D}^{20·2°}$ 1·4413, whence $[R_L]_D$ = 65·59 (calc. for normal ester, 65·55) (Found: C, 60·0; H, 8·5. Calc.: C, 60·4; H, 8·5%); its semicarbazone melts at 76° (Found: C, 52·8; H, 7·9. Calc.: C, 53·3; H, 7·9%). The same ester is obtained when the original condensation product is hydrolysed with alcoholic hydrogen chloride.

Oxidation of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid.—The acid (10 g.) is dissolved in 40 c.c. of 10% sodium hydroxide solution and added to a solution of hypobromite (Br, 12 c.c.; H_2O, 150 c.c.; 10% NaOH soln., 200 c.c.), cooled in ice. After 1½ hours, the bromoform is extracted with ether and the alkaline solution is treated with sulphur dioxide, acidified with hydrochloric acid, and saturated with ammonium sulphate. Ether then extracts α-carboxy-ββ-dimethylglutaric acid (XIV), m. p. 173° (decomp.) (compare Perkin and Goodwin, *loc. cit.*).

Behaviour of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid (V) *on Heating.*—The acid (5 g.) was heated in a bath at 130—140° for 5 hours. An ethereal solution of the cooled melt, when shaken with dilute sodium carbonate solution, dried, and evaporated, left 1·15 g. (equivalent to 25% of the dibasic acid) of the dilactone (XVI); the alkaline extract gave on acidification a quantity of the acid (XVII) representing 72% of the dibasic acid: 97% of the total material is thus accounted for.

Different quantities of the dibasic acid were heated in this way, but the weight of dilactone isolated always represented 25—27% of the dibasic acid.

γ-Acetyl-ββ-dimethylbutyric acid (XVII), obtained as described above, is a somewhat viscous liquid, b. p. 162°/25 mm., $d_{4°}^{19·3°}$ 1·03646, $n_{D}^{19·3°}$ 1·44652, whence $[R_L]_D$ = 40·6 (calc., 40·69) (Found for the *silver* salt: Ag, 40·4. $C_8H_{13}O_3Ag$ requires Ag, 40·7%). The semicarbazone melts at 172° (decomp.) (compare Vorländer and Gärtner, *loc. cit.*).

The ethyl ester (XXV) is obtained by the alcohol–hydrogen chloride method as a colourless mobile liquid with a rather characteristic odour, b. p. 112°/17 mm., $d_{4°}^{19·8°}$ 0·96248, $n_{D}^{19·8°}$ 1·43047, whence $[R_L]_D$ = 49·97 (calc. for the normal ester, 50·05) (Found: C, 64·4; H, 9·6. Calc.: C, 64·5; H, 9·7%); its semicarbazone crystallises from dilute methyl alcohol in lustrous flat needles, m. p. 114° (Found: C, 54·6; H, 9·3. Calc.: C, 54·3; H, 8·6%).

Synthesis of Ethyl γ-Acetyl-ββ-dimethylbutyrate (XXV).—ββ-Dimethylglutaric anhydride is heated with twice the calculated

quantity of absolute alcohol on the steam-bath for 3—4 hours; the excess of alcohol is then removed under reduced pressure and water added. The precipitated oil is taken up in ether and shaken with sodium carbonate solution. The alkaline solution on acidification gives *ethyl hydrogen* ββ-*dimethylglutarate*, which is dissolved in ether, dried, and distilled in a vacuum; b. p. 164°/16 mm., $d_4^{18 \cdot 1^\circ}$ 1·05574, $n_D^{18 \cdot 1^\circ}$ 1·4403, whence $[R_L]_D$ = 46·97 (calc., 46·95) (Found for the *silver* salt: Ag, 36·6. $C_9H_{15}O_4Ag$ requires Ag, 36·6%).

This ester (40 g.) and thionyl chloride (36 c.c.) are heated on the steam-bath for an hour and the product is distilled in a vacuum; the acid chloride is obtained as a colourless mobile liquid (41 g.), b. p. 117°/16 mm.

A well-cooled benzene solution of zinc methyl iodide obtained from 55 g. of zinc–copper couple, 44 c.c. of methyl iodide, 21 c.c. of ethyl acetate, and 50 c.c. of benzene is diluted with 100 c.c. more of the dry solvent and the acid chloride (41 g.) in dry benzene (30 c.c.) is slowly added. After 1 hour, the excess of zinc methyl iodide is decomposed with ice and dilute sulphuric acid, and the benzene solution is washed with water, dilute sodium hydroxide solution, and again with water and then dried and fractionated in a vacuum; the keto-ester (XXV) distils at 126—128°/13 mm. After purification through the semicarbazone it has b. p. 113°/18 mm., $d_4^{20 \cdot 9^\circ}$ 0·96323, $n_D^{20 \cdot 9^\circ}$ 1·43067, whence $[R_L]_D$ = 49·95 (Found: C, 64·4; H, 9·9%). The semicarbazone prepared from it (Found: C, 54·1; H, 8·6%) melts at 114°, alone or mixed with the semicarbazone of the ester from the acid (XVII).

*Action of Acetyl Chloride on γ-Acetyl-*ββ*-dimethylbutyric Acid.*—After a mixture of the acid (XVII) (15 g.) and acetyl chloride (13 c.c.) has been kept at the ordinary temperature for 2 days, the solution is poured on ice and the oil is extracted with ether, washed with dilute sodium carbonate solution, dried, and distilled. A colourless, mobile liquid with the characteristic odour of the unsaturated lactone (XXVIII) is obtained, b. p. 82°/10 mm., $d_4^{22 \cdot 2^\circ}$ 0·98658, $n_D^{22 \cdot 2^\circ}$ 1·45573, whence $[R_L]_D$ = 38·55 (calc., 38·13) (Found: C, 68·6; H, 9·0. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·6%) (compare Bredt, *Annalen*, 1898, **299**, 179).

Preparation of ββδ*-Trimethylvalerolactone* (XXIX).—The acid (XVII) (10 g.) is reduced with sodium (11 g.) and boiling absolute alcohol (185 c.c.) and after 2½ hours' heating the alcohol is distilled in steam, the residue acidified with concentrated hydrochloric acid, and the oil extracted with ether, washed with sodium carbonate solution, dried, and distilled. The *lactone* (6·6 g.), a colourless mobile liquid with a faint lactonaceous odour, has b. p. 120°/18 mm., d_4

0·98039, $n_D^{17^\circ}$ 1·44743, whence $[R_L]_D$ = 38·73 (calc., 38·70) (Found: C, 67·1; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6; H, 9·8%).

In conclusion, the author wishes to acknowledge his indebtedness to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in this investigation and to the Government of Bengal for a foreign scholarship and a grant towards the purchase of chemicals. The author also desires to thank Dr. J. C. Bardhan of this laboratory for his friendly advice.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, November 6th*, 1928.]

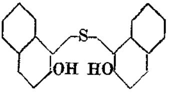
XXIX.—*A Synthesis of* iso*Naphthathioxin.*

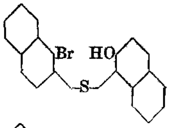
By AARON COHEN and SAMUEL SMILES.

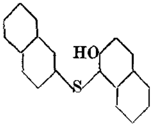
DEHYDRATION of 2-naphthol 1-sulphide (I) gives αβα′β′-naphthathioxin (Mauthner, *Ber.*, 1906, **39**, 1346), and similar treatment of *iso*-β-naphthol sulphide yields *iso*naphthathioxin (J., 1913, **103**, 347, 909), which is also obtained from dehydro-β-uaphthol sulphide by means of acetyl iodide (J., 1914, **105**, 1741). For many reasons which need not be here enumerated, the constitutions assigned to *iso*-β-naphthol sulphide (Lesser and Gad, *Ber.*, 1923, **56**, 963) and to dehydro-β-naphthol sulphide (Hinsberg, *J. pr. Chem.*, 1915, **91**, 307) are unsatisfactory. In seeking further information concerning them it seemed necessary as a first step to determine the structure of *iso*naphthathioxin, since this substance is simply related to both. αβα′β′-Naphthathioxin being known, syntheses of the αββ′α′- and βαβ′α′-derivatives were required for comparison of these materials with *iso*naphthathioxin. A preliminary account of experiments directed to the synthesis of αββ′α′-naphthathioxin has already been communicated (J., 1926, 957), since attempts having the same object were recorded elsewhere (Lesser and Gad, *Ber.*, 1925, **58**, 2557) while the work was in progress.

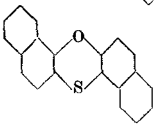
All attempts to sulphurate 1 : 2′-dinaphthyl oxide having failed, di-1-iodonaphthyl 2-disulphide was heated with sodium 2-naphthoxide in presence of copper; but the expected 2-disulphide of 1 : 2′-dinaphthyl oxide was not obtained, the only definite product encountered being the dinaphthathianthren which results from the action of copper on the disulphide alone (J., 1928, 1149). Attention was therefore directed to the derivatives of 1 : 2′-dinaphthyl sulphide. Dehydration of a 2 : 1′-dihydroxy-derivative (J., 1926, 957) was tried without success, but it was expected that halogen acid might

be removed from 1-bromo-2′-hydroxy-2 : 1′-dinaphthyl sulphide (II).

(I.) 

 (II.)

(III.) 

 (IV.)

Previous experience (J., 1926, 1723) had shown that 2′-hydroxy-2 : 1′-dinaphthyl sulphide (III) is smoothly formed from sodium 2-naphthoxide and 2-naphthyl disulphoxide. 1-Bromonaphthalene-2-sulphinic acid was therefore prepared from 1-bromo-β-naphthylamine or from α-naphthylamine-2-sulphonic acid by the usual methods, but the conversion of this acid into the required disulphoxide could not be effected, the corresponding disulphide being obtained when the usual reagents were employed. Bromination of 2-naphthyl disulphoxide in acetic acid also gave this disulphide owing to reduction by the hydrogen bromide liberated (compare Fries, *Ber.*, 1914, **47**, 1196), but even when this was avoided by operating in pyridine the chief product was 2-naphthyl disulphide. Evidently before bromination took place the thiolsulphonate group was ruptured. Finally it was found that careful bromination of the hydroxy-sulphide (III) led to the desired material (II). The situation of halogen in this product was proved by synthesis, though in poor yield and quality, from the fusion of β-naphthol and 1-bromonaphthalene-2-sulphinic acid according to a reaction studied by Hinsberg (*Ber.*, 1903, **36**, 108) in other simpler cases. When the sodium derivative of this bromohydroxy-sulphide (II) was heated in presence of copper acetate a good yield of the required αββ′α′-naphthathioxin (IV) was isolated; this product was identical with the *iso*naphthathioxin obtained from *iso*-β-naphthol sulphide or from the dehydro-derivative.

It is evident that this result has an important bearing on the structures to be assigned to the "iso-" and "dehydro-" sulphides, but a discussion of this question is deferred until further evidence has been collected from experiments now in progress. One interesting feature which is now clear in the relations between these sub-

stances is that during the conversion of 2-naphthol 1-sulphide (I) *via* the dehydro-sulphide into the αββ'α'-naphthathioxin (IV) the situations of oxygen and sulphur in one naphthalene nucleus have become interchanged.

EXPERIMENTAL.

1-*Bromonaphthalene-2-sulphinic Acid*, $C_{10}H_6Br{\cdot}SO_2H$.—(a) *From α-naphthylamine-2-sulphonic acid.* The moist diazo-compound prepared as usual from the amino-acid (25 g.) was gradually added to a boiling solution of cuprous bromide (10 g.) in hydrobromic acid (100 c.c. of 36 %). When reaction was complete, the bromosulphonic acid was collected from the cooled liquid and purified by recrystallisation (charcoal) of the sodium salt (yield, 50%). This was converted into the sulphonyl chloride by treatment (20 g.) with an equal weight of phosphorus pentachloride (1 hour). 1-*Bromonaphthalene-2-sulphonyl chloride* separated from acetic acid in needles, m. p. 93—94° (Found: Cl + Br, 37·8. $C_{10}H_6O_2ClBrS$ requires Cl + Br, 37·8%). When this sulphonyl chloride was shaken (1 hour) with a concentrated alkaline solution of sodium sulphite it dissolved and from the clear solution sulphuric acid (60%) liberated the required sulphinic acid (yield, 60%).

(b) *From* 1-*bromo-β-naphthylamine.* The hydrochloride of the base (10 g.) was suspended in hydrochloric acid (100 c.c. of 15%) and diazotised at 0° (3 g. of sodium nitrite in 25 c.c. of water). The clear solution was slowly added to a stirred mixture of copper paste (50 g.) and a saturated solution of sulphur dioxide (150 c.c.), a current of the gas being maintained during the process. When decomposition was complete the solid was mixed with aqueous sodium hydroxide. The purified solution (charcoal) of the sodium salt was mixed with sulphuric acid (60 %), the required *sulphinic acid* being liberated (yield, about 60%). The sulphinic acid obtained by these methods was very sparingly soluble in water; it separated from aqueous acetone in needles, m. p. 146° (Found: C, 44·4; H, 2·4. $C_{10}H_7O_2BrS$ requires C, 44·3; H, 2·6%). When dissolved in pure warm thionyl chloride it yielded a relatively stable chloride 1-*Bromonaphthalene-2-sulphinyl chloride*, $C_{10}H_6Br{\cdot}SOCl$, separated from dry benzene in yellow prisms, m. p. 110° (Found: Cl + Br, 39·7. $C_{10}H_6OClBrS$ requires Cl + Br, 39·9%).

Di-1-*bromonaphthyl* 2-*Disulphide*, $(C_{10}H_6Br{\cdot}S{\cdot})_2$.—A solution of the sulphinic acid in hot alcohol was saturated with sulphur dioxide and mixed with a few drops of hydriodic acid (*d* 1·7). Reduction was soon complete, the required *disulphide* separating from the liquid (yield, 90%). It was very sparingly soluble in alcohol or acetic acid and separated in plates, m. p. 161°, from benzene

acetic acid (Found: C, 50·1; H, 2·6; *M*, 461. $C_{20}H_{12}Br_2S_2$ requires C, 50·4; H, 2·5%; *M*, 476). This disulphide was also obtained in almost quantitative yield by slowly adding a solution of bromine in acetic acid to 2-naphthyl disulphoxide in the same solvent.

1-*Bromo-2'-hydroxydinaphthyl* 2 : 1'-*Sulphide* (II).—(a) Acetic acid containing the theoretical amount of bromine was slowly added to a warm solution of 2'-hydroxydinaphthyl 2 : 1'-sulphide (III) in the same solvent. The reaction, which began at once, was completed by warming the mixture (50°). The product (yield, 95%), isolated by addition of water, crystallised from acetic acid (charcoal) in leaflets, m. p. 154° (Found: C, 62·7; H, 3·6. $C_{20}H_{13}OBrS$ requires C, 63·0; H, 3·4%).

(b) A molten mixture of 1-bromonaphthalene-2-sulphinic acid (5 g.) and β-naphthol (2·6 g.) was kept at 95—100° during 2½ hours. The dark violet product was boiled with dilute aqueous sodium hydroxide (8%), and the hot solution, freed from a small quantity of insoluble material, was mixed with a suitable amount of sodium hyposulphite (charcoal). On cooling, the sodium derivative of the required naphthol separated in the crystalline state (2·2 g.); it was purified from hot dilute sodium hydroxide solution. The naphthol generated from this salt and purified as previously indicated had m. p. 154° and this was not depressed by mixture with a sample obtained by bromination (method a). The substance gave a green solution in warm sulphuric acid. The sparingly soluble sodium salt separated from hot water in small shining plates. This bromonaphthol sulphide occurs in two forms. Sometimes method (a) yielded a product which after purification had m. p. 135—136°; but the molten substance resolidified a few degrees above this and finally melted at 154°. Mixture of this material (m. p. 135°) with that of m. p. 154° did not depress this m. p. More precise conditions of the relative stability of these materials were not determined.

1-*Bromo-2'-acetoxydinaphthyl* 2 : 1'-*sulphide*, prepared from the foregoing hydroxy-compound and acetic anhydride, was purified from dilute acetic acid. When rapidly separated from this medium, it was obtained in the amorphous state, but if allowed to separate slowly from dilute solution it formed needles, m. p. 116—117° (Found: C, 62·4; H, 3·5. $C_{22}H_{15}O_2BrS$ requires C, 62·4; H, 3·5%).

αββ'α'-*Naphthathioxin* (IV).—A mixture of the dry sodium derivative of 1-bromo-2'-hydroxydinaphthyl 2 : 1'-sulphide (II), obtained by either of the methods described, and a little copper acetate was heated under diminished pressure (1 mm.). Reaction began at 140—150°, the mixture then became pasty and the product slowly sublimed. The process was more rapid at 160—170° (yield,

ca. 50%). The crude sublimed product had m. p. 151—152°, and after purification from alcohol was obtained in yellow needles, m. p. 154° (Found: C, 79·8; H, 4·2. Calc.: C, 80·0; H, 4·0%). This material did not depress the melting point of a sample of *iso*naphthathioxin obtained from the sources already mentioned. The identification was also effected by comparison of the picrates (m. p. 177—178°) and dibromo-derivatives (m. p. 245°) of these materials.

In conclusion we desire to thank Dr. Child for information concerning 1-bromonaphthalene-2-sulphonic acid and its derivatives.

KING'S COLLEGE, LONDON. [*Received, December 5th, 1928.*]

NOTES.

The Formation of Liesegang Rings as a Periodic Coagulation Phenomenon. By JACK REGINALD IRONS HEPBURN.

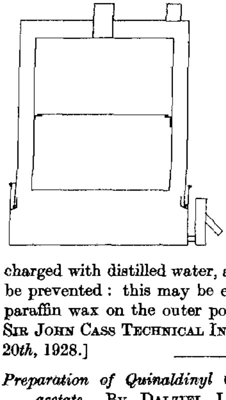
IN a paper with the above title (J., 1928, 2714) Hedges and Henley have provided experimental evidence in support of an hypothesis advanced originally by Freundlich ("Colloid and Capillary Chemistry," p. 735), although they make no reference to his views.

Previous to the publication of the above paper, the author had carried out experiments with the object of testing the coagulation theory of the production of periodic structures. For instance, in connexion with his study of the formation of malachite (J., 1925, **127**, 1008), basic cupric carbonate was formed by admixture of a solution of 0·1*N*-copper sulphate and 10% gelatin, with an equal volume of 0·1*N*-sodium carbonate and 10% gelatin. The product was a green, transparent, slightly opalescent gel, instead of the ordinary blue flocculent precipitate. The set gel was covered with *N*-sodium carbonate solution, which was allowed to diffuse into it. After a week, three intensely violet rings had appeared, and the number had increased to thirteen after three weeks. When, however, *N*-copper sulphate solution was used as coagulant, only one light green band was produced, after which diffusion ceased.

The production of stratified formations by the coagulation of sols has been studied by Quincke (*Ann. Physik*, 1902, **9**, 987), who describes the coagulation of an arsenic trisulphide hydrosol—unprotected by gelatin—by diffusion of solutions of ferric chloride and of aluminium sulphate. He mentions the production of layers after flocculation, richer and poorer in flocks, with horizontal or convex surfaces.—NORTHERN POLYTECHNIC, LONDON, N. 7. [*Received, November 17th, 1928.*]

A Steam Drying Oven with Detachable Base. By HENRY J. S. SAND.

THE base of this oven is constructed as a separate unit distinct from the rest, the junction between the two parts being made by a hydraulic seal (see fig.). This is effected by fitting the top of the base with a gutter, which is maintained full of water by condensation from the walls of the oven, the excess overflowing into the base. The general construction will be apparent from the section shown. The device is useful for small laboratory steam-ovens, since the base can be readily freed from scale, and renewed if necessary. It is, however, particularly valuable for larger combined ovens and stills. For these, the top of the oven is fixed rigidly to a stand, the base being supported on two cranked rods, to which handles are attached, by the turning of which the base may be instantly lowered and removed for cleaning. In ovens which are fitted with a reflux condenser and water gauge and are charged with distilled water, all loss of water by evaporation should be prevented: this may be effected by floating a small amount of paraffin wax on the outer portion of the water forming the seal.—SIR JOHN CASS TECHNICAL INSTITUTE, E.C. 3. [*Received, November 20th*, 1928.]



Preparation of Quinaldinyl Chloride and Ethyl Quinaldinylacetoacetate. By DALZIEL LLEWELLYN HAMMICK and WILLIAM P. DICKINSON.

QUINALDINYL chloride was first prepared by Meyer (*Monatsh.*, 1904, **25**, 1199; *Ber.*, 1905, **38**, 2488) by the action of thionyl chloride on the acid and described as a very sparingly soluble, crystalline substance of m. p. 175—176°. Besthorn and Ibele subsequently (*Ber.*, 1905, **38**, 2127) claimed to have obtained, also by the action of thionyl chloride on the acid, an acid chloride of m. p. 96° and readily soluble in organic solvents. Meyer's inability to obtain Besthorn's product was ascribed by Besthorn (*Ber.*, 1908, **41**, 2003) to the presence of anticatalysts (notably tin) in the thionyl chloride used. With Meyer's demonstration (*loc. cit.*) that Besthorn's criticisms were unfounded, the problem of the preparation of the soluble form of the acid chloride appears to have been left unsolved, the position being that the compound has only been prepared in one laboratory.

We have attempted to prepare the low-melting acid chloride according to the directions of Besthorn and Ibele (*loc. cit.*; *Ber.*, 1906, **39**, 2329) and confirm the observations of Meyer that the high-melting form is invariably obtained (Found: Cl, 18·0. Calc.: Cl, 18·5%), even when the purest thionyl chloride is used after redistillation from several successive quantities of quinaldinic acid. We have, however, obtained an acid chloride of m. p. 97° in two ways: (*a*) 12 G. of quinaldinic acid, freshly crystallised from ligroin of b. p. 100—120° (this crystallisation is essential for success), were suspended in 300 c.c. of ligroin (b. p. 100—120°), and 12·4 g. of phosphorus pentachloride added. The mixture was boiled under reflux until evolution of hydrogen chloride ceased and the liquid went clear. Large needle-shaped crystals of the acid chloride, m. p. 97°, separated on cooling. Yield, 7·5 g. or 60% (Found: Cl, 18·7%).

(*b*) Ethyl quinaldinate (fine needles, m. p. 36°, prepared by boiling the acid in ethyl alcohol containing sulphuric acid) (0·5 g.) was dissolved in 40 c.c. of ligroin (b. p. 100—120°), and 0·5 g. of phosphorus pentachloride added. Crystals of the acid chloride began to separate at once and, after stirring for an hour at room temperature, 0·45 g. of the low-melting form was obtained (yield, nearly theoretical).

The high- and the low-melting acid chloride, on treatment with water, each gave only hydrochloric and quinaldinic acids.

Ethyl Quinaldinylacetoacetate, $CH_3\cdot CO\cdot CH(CO\cdot C_9H_6N)\cdot CO_2Et$.—To the suspension produced by cooling a solution of 2·4 g. of sodium and 13·6 g. of ethyl acetoacetate in 200 c.c. of dry warm benzene, 10 g. of quinaldinyl chloride (m. p. 97°), dissolved in 300 c.c. of dry benzene, were added and the mixture was shaken for 24 hours. The solid product was then collected, washed with ether, dissolved in water, and acidified with dilute acetic acid. The oil that separated, after being dried in ether with anhydrous sodium sulphate, solidified on standing and was recrystallised twice from ligroin (b. p. 60—80°); m. p. 61° (Found: N, 4·8. $C_{16}H_{15}O_4N$ requires N, 4·9%). Yield, 30%. On treatment with copper acetate in aqueous alcohol it gave a copper derivative, m. p. 178° (decomp.), that was readily soluble in alcohol, benzene, and chloroform.

All attempts to prepare ethyl quinaldinylacetate from the acetoacetic ester failed. Dry ammonia in ether (Bouveault and Bougert, *Bull. Soc. chim.*, 1902, **27**, 1088) gave a quantitative yield of quinaldinamide. Cold ammonia and ammonium chloride (Perkin and Needham, J., 1904, **85**, 148) had no effect; at 50° the amide was again obtained.—THE DYSON PERRINS LABORATORY, OXFORD.

[*Received, December 1st, 1928.*]

The Council has ordered the following Report and Table to be printed in the Journal.

Revised Table of Atomic Weights for 1929.

The annual publication by the International Committee on Atomic Weights of their revised tables of atomic weights, esteemed by chemists as authoritative estimates of the most probable values, ceased with the issue of the table for 1921 by F. W. Clarke, T. E. Thorpe, and G. Urbain (J., 1920, **117**, 885). In 1925 a table prepared by the International Committee on the Chemical Elements, appointed by the International Union of Pure and Applied Chemistry, was published (J., 1925, **127**, 913), but since then no revised table of atomic weights has been published in Great Britain. Therefore, to meet a general need, the Council of the Society appointed a Sub-Committee on Atomic Weights to prepare a revised table for 1929.

Because so long a period has elapsed since the last revision, the task of the Committee has been unusually heavy and has involved a detailed examination of the very considerable amount of work published on atomic weights since 1919, to review which adequately here is hardly practicable. Fortunately this is unnecessary, as the data have been adequately summarised both in the Annual Reports of the German Commission on Atomic Weights published in the *Berichte*, and in the Reports by Professor G. P. Baxter published annually in the *Journal of the American Chemical Society*. We proceed, therefore, simply to outline the main principles governing the preparation of the new table.

The whole of the work on atomic weights published up to 1919 was very thoroughly discussed by F. W. Clarke in his "Recalculation of the Atomic Weights," published by the Smithsonian Institution in that year. Being satisfied that Clarke's method of computation from the available data is sound and trustworthy, we have adopted his final values for those elements, 36 in number, for which no determinations have since been published. These elements are as follows:

Li Mg S Ca V Cr Mn Kr Rb Sr Nb Mo Ru Rh Pd In Xe Cs Ba
Ce Pr Nd Eu Gd Tb Yb La Ta W Os Ir Pt Au Tl Nt Ra

Clarke's figures for the other elements have been modified in accordance with more recent work to obtain the values now given.

For the nine "simple" elements H, He, C, N, F, Na, P, As, and

I the values obtained by F. W. Aston with his new mass-spectrograph are adopted in preference to those deduced from the "physical" or "chemical" data, because we are of opinion that, in these cases, Aston's method is less liable to error than any other. This opinion is strengthened by the agreement observed between the measured and the calculated differences of these values from whole numbers (see "packing-fractions"; F. W. Aston, *Proc. Roy. Soc.*, 1927, **A**, **115**, 487), and their adoption is further justified by the consideration that it does not materially alter the figures deduced by other methods save in one case, that of phosphorus, where the "chemical" data are discordant and obviously unsatisfactory.

In recent years the fundamental importance of the atomic numbers has become so apparent that the present table gives the elements in the order of those numbers. This has the advantage of permitting the inclusion of those elements which are as yet undiscovered and also the known elements for which no determinations of atomic weight are available. It is felt that in so short a list no difficulty should arise in finding an element by name when that is necessary.

Where definite information is available the mass-numbers of the known isotopes of the elements are also given, in the order of their abundance as deduced from the relative intensities of the lines in the mass-spectrum.

In stating the atomic weights use has been made of the convenient device of writing the last figure as a subscript in those cases where it may be in error by two or three units. Where the last figure is not differentiated it is to be understood that in our opinion the error probably does not exceed one unit.

(Signed) F. W. ASTON.
H. V. A. BRISCOE.
R. WHYTLAW GRAY.
E. K. RIDEAL.

1929.

ATOMIC WEIGHTS.

Where the last figure of an atomic weight may be in error by sever units it is given as a subscript figure. Where the last figure is given i ordinary type its error probably does not exceed one, or at most two, unit

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
1	Hydrogen	H	1·0078	1
2	Helium	He	$4{\cdot}002_2$	4
3	Lithium	Li	6·94	7, 6
4	*Beryllium*	Be	9·02	9
5	Boron	B	10·83	11, 10
6	Carbon	C	$12{\cdot}003_6$	12
7	Nitrogen	N	14·008	14
8	Oxygen	O	16·0000	16
9	*Fluorine*	F	19·00	19
10	Neon	Ne	20·18	20, 22, 21
11	Sodium	Na	23·000	23
12	Magnesium	Mg	24·30	24, 25, 26
13	Aluminium	Al	$26{\cdot}97_0$	27
14	Silicon	Si	$28{\cdot}0_8$	28, 29, 30
15	Phosphorus	P	$30{\cdot}98_2$	31
16	Sulphur	S	$32{\cdot}06_5$	32, 33, 34
17	*Chlorine*	Cl	35·457	35, 37
18	Argon	A	39·94	40, 36
19	Potassium	K	$39{\cdot}10_5$	39, 41
20	Calcium	Ca	40·09	40, 44
21	Scandium	Sc	$45{\cdot}1_5$	45
22	Titanium	Ti	47·90	48
23	Vanadium	V	50·95	51
24	Chromium	Cr	52·04	52
25	Manganese	Mn	54·95	55
26	Iron	Fe	55·84	56, 54
27	Cobalt	Co	58·95	59
28	Nickel	Ni	58·69	58, 60
29	Copper	Cu	63·55	63, 65
30	Zinc	Zn	65·38	64, 66, 68, 67, 65, 70, 69
31	Gallium	Ga	69·72	69, 71
32	Germanium	Ge	72·60	74, 72, 70, 73, 75, 76, 71, 77
33	Arsenic	As	$74{\cdot}93_4$	75
34	Selenium	Se	79·2	80, 78, 76, 82, 77, 74
35	Bromine	Br	$79{\cdot}91_5$	79, 81
36	Krypton	Kr	82·9	84, 86, 82, 83, 80, 78
37	Rubidium	Rb	$85{\cdot}4_3$	85, 87
38	Strontium	Sr	$87{\cdot}6_3$	88, 86
39	Yttrium	Yt	$88{\cdot}9_3$	89
40	Zirconium	Zr	91·2	90, 94, 92, (96)
41	Niobium (Columbium)	Nb (Cb)	93·3	
42	Molybdenum	Mo	96·0	
43	Masurium	Ma	—	
44	Ruthenium	Ru	$101{\cdot}6_5$	
45	Rhodium	Rh	102·9	
46	Palladium	Pd	106·7	
47	Silver	Ag	107·880	107, 109

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
48	Cadmium	Cd	$112{\cdot}4_0$	114, 112, 110, 113, 111, 116
49	*Indium*	*In*	114·8	*115*
50	Tin	Sn	118·70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
51	Antimony	Sb	121·76	121, 123
52	Tellurium	Te	127·5	128, 130, 126
53	Iodine	I	$126{\cdot}93_2$	127
54	Xenon	Xe	130·2	129, 132, 131, 134, 136, 128, 130, 126, 124
55	Cæsium	Cs	$132{\cdot}8_1$	133
56	Barium	Ba	$137{\cdot}3_6$	138
57	Lanthanum	La	$138{\cdot}9_0$	139
58	*Cerium*	*Ce*	*140·2*	*140, 142*
59	Praseodymium	Pr	140·9	141
60	Neodymium	Nd	$144{\cdot}2_5$	142, 144, 146, (145)
61	Illinium	Il	—	
62	Samarium	Sm	$150{\cdot}4_3$	
63	Europium	Eu	152·0	
64	Gadolinium	Gd	157·0	
65	Terbium	Tb	159·2	
66	*Dysprosium*	*Dy*	$162{\cdot}4_6$	
67	Holmium	Ho	163·5	
68	*Erbium*	*Er*	167·6	
69	Thulium	Tm	169·4	
70	Ytterbium	Yb	$173{\cdot}_0$	
71	Lutecium	Lu	$175{\cdot}_0$	
72	Hafnium	Hf	178·6	
73	Tantalum	Ta	181·3	
74	*Tungsten*	W	184·1	
75	Rhenium	Re	—	
76	Osmium	Os	$191{\cdot}_0$	
77	*Iridium*	*Ir*	$193{\cdot}0_4$	
78	Platinum	Pt	195·2	
79	Gold	Au	$197{\cdot}2_1$	
80	Mercury	Hg	$200{\cdot}6_0$	202, 200, 199, 198, 201, 204, 196
81	Thallium	Tl	$204{\cdot}_3$	
82	Lead	Pb	$207{\cdot}2_2$	208, 206, 207
83	Bismuth	Bi	$209{\cdot}0_0$	
84	Polonium	Po	—	
85	—	—	—	
86	Niton (Emanation)	Nt (Em)	222	
87	—	—	—	
88	Radium	Ra	$225{\cdot}9_5$	
89	Actinium	Ac	—	
90	Thorium	Th	232·15	
91	Protoactinium	Pa	—	
92	Uranium	U	$238{\cdot}1_5$	

XXX.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part IV. The Hydrogenation of Conjugated Systems : Piperic Acid.*

By SERGUEY V. LEBEDEV and ANASTASIA O. YAKUBCHIK.

ACCORDING to our theory of the catalytic hydrogenation of conjugated systems (J., 1928, 823), we should expect that, if piperic acid were hydrogenated by the direct addition of 2 mols. of hydrogen, the curve representing the process would be similar to that of the hydrogenation of a monoethylenic compound and would show no discontinuity, and the reaction product at any stage during the course of the reaction would consist solely of the fully saturated and the initial compound. Paal, who investigated this reduction (*Ber.*, 1912, **45**, 2221), found no indication of the presence of dihydropiperic acid, and hence the process would appear to conform to Type III of our classification (*loc. cit.*).

We have now repeated this reduction, however, and have found that in alcoholic solution in presence of platinum black, considerable quantities of dihydropiperic acid are formed; moreover, a "critical point" was found at 76% hydrogenation, and hence the process conforms to our Type II. The contradiction might have been attributed to the difference in the conditions of the process as carried out by Paal and by ourselves, but when we repeated the reduction under Paal's conditions (*i.e.*, in aqueous solution and in presence of colloidal palladium), the results were the same, dihydropiperic acids being produced in even larger amounts than before, and the critical point then being at 68—70% of the total hydrogen required.

We therefore suggest that the material extracted by ligroin in Paal's experiments was not pure tetrahydropiperic acid but contained more than 50% of the dihydro-acid, and our contention is supported by Paal's analytical results.

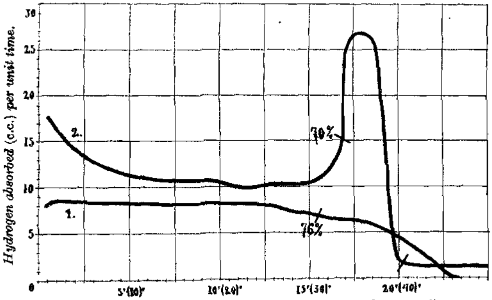
EXPERIMENTAL.

Hydrogenation in Presence of Platinum Black.

Piperic acid, obtained by saponification of piperine (Fittig and Milk, *Annalen*, 1869, **152**, 28) and recrystallised from alcohol, had m. p. 215—216·5°. 1·4338 G. of the acid, with 1·0 g. of platinum black in 250 c.c. of alcohol at 11°, absorbed 309 c.c. of hydrogen (at 18° and 765 mm.); the slight break in the curve showing the progress of absorption (Curve 1, Fig. 1) indicates a critical point at 75—77% of the total hydrogen absorbed.

The formula of piperic acid, $CH_2O_2{:}C_6H_3{\cdot}\overset{\delta}{C}H{:}\overset{\gamma}{C}H{\cdot}\overset{\beta}{C}H{:}\overset{\alpha}{C}H{\cdot}CO_2H$, indicates the following possibilities for the hydrogenation : (1) Addition of 1 mol. of hydrogen in one of the positions $\gamma\delta$, $\alpha\beta$, $\alpha\delta$, to give three isomeric dihydro-acids. (2) Addition of 2 mols. to 1 mol. of the acid, giving tetrahydropiperic acid. Thus, on the curve showing the course of hydrogenation we can expect only two sections : one during which the conjugated system is hydrogenated, and the second corresponding to the saturation of the dihydropiperic acids thus formed. The three different dihydro-acids, being symmetrical disubstituted ethylenic compounds, hydrogenate simultaneously (see J., 1925, **127**, 417), and hence are represented by a single section

FIG. 1.



Time (in minutes for curve 1, *and in* ½ *minutes for curve* 2).

1. *Authors' method.* 2. *Paal's method.*

on the hydrogenation curve. The curve therefore shows that the process does not proceed as supposed by Paal, and that the hydrogenation is of our Type II.

To confirm this we examined the product of 50% hydrogenation of the acid, 1·7569 g. in 450 c.c. of alcohol having absorbed 191 c.c. (at 18° and 760 mm.) (1 mol.) of hydrogen in presence of 1 g. of platinum black. The acids (1·7731 g.) isolated from alcohol were extracted by ligroin, in which, as shown by control experiments, piperic acid is insoluble, whereas the reduced acids are readily soluble. In this way 0·596 g. of piperic acid (m. p. 209—211°) was separated, corresponding to 33·6% of unchanged acid in the product of hydrogenation; hence, since 50% of the possible amount of hydrogen has been absorbed, the amount of tetrahydro-acid must

also be 33·6% (see J., 1928, 825), and that of dihydro-acids 32·8% (by difference) (see Table I), from which, by methods explained in Part II (*ibid.*, p. 826), we find that the critical point falls at 75% of hydrogenation. The ligroin solution yielded 1·2320 g. of mixed di- and tetra-hydro-acids (m. p. 88—96°).

TABLE I.

Composition of the 50% hydrogenation product (platinum-black method).

	Calc. from amount of piperic acid.	Calc. from amount of dihydropiperic acids.	Mean.
Piperic acid	33·6%	35·0%	34·3%
Tetrahydropiperic acid......	33·6	35·0	34·3
Dihydropiperic acids	32·8	30·0	31·4
Total	100	100	100

Examination of Mixed Di- and Tetra-hydro-acids.—2·5296 G. of the mixed acids thus obtained were dissolved in 35 c.c. of alcohol and treated with hydrogen in the presence of 1·2 g. of platinum black, 125·5 c.c. (at 15° and 755 mm.) being absorbed. If the mixture had consisted entirely of dihydro-acids, 272·5 c.c. of hydrogen would have been required under these conditions; hence, the composition of the mixture was 46% of the dihydro- and 54% of the tetrahydro-acid, and the composition of the original 50% hydrogenation mixture as calculated from these data is shown in the second column of Table I,* corresponding to a critical point at 77% hydrogenation.

Fig. 2 is based upon a critical point at 76% hydrogenation—the mean of the values found by the three methods above. The diagram for piperic acid hydrogenation is thus very similar to that of divinyl (see Part III, J., 1928, 2190), for the position of the critical point is nearly the same in each case; and all the criteria allocate the process to our Type II.

Hydrogenation of Piperic Acid in Presence of Colloidal Palladium.

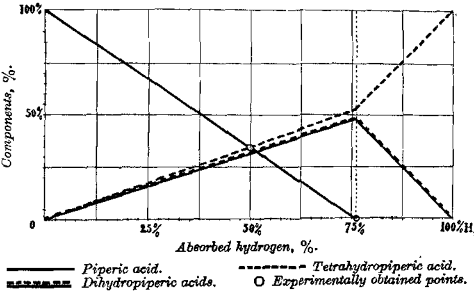
Total Hydrogenation.—2·5121 G. of piperic acid, suspended in 90 c.c. of water and neutralised by potassium hydroxide, were hydrogenated with 0·0147 g. of colloidal palladium, previously saturated with hydrogen; 555 c.c. (at 18° and 750 mm.) of gas were required for total hydrogenation (calc., 557 c.c.). The course of the process is represented by Curve 2, Fig. 1: the curve has a sharp break and

* The lower proportion of dihydro-acids in the hydrogenation product (*viz.*, 30% instead of 32·8%) is attributed to partial oxidation during recrystallisation.

a peculiar shape, and the critical point is at 70% of hydrogen absorbed.

50% *Hydrogenation.*—5·0073 G. of the acid in 75 c.c. of water were hydrogenated as above in presence of 0·05 g. of catalyst; 550·5 c.c. (at 17° and 754 mm.) were absorbed (calc., 550·5 c.c.). The acids were precipitated by dilute sulphuric acid, washed, dried, and extracted by alcohol, from which 4·9691 g. of mixed acids crystallised. Treatment with ligroin as above isolated 1·2464 g. of piperic acid (m. p. 207—209°), corresponding to 25% of unchanged acid. From the ligroin solution 3·7229 g. of soluble acids (m. p. 90—116°) were obtained, and 3·1312 g. of these were hydrogenated with 0·0065 g. of colloidal palladium as before. Since

Fig. 2.



211 c.c. (at 20° and 760 mm.) of hydrogen were required as compared with a possible 341 c.c., it follows that 61·9% of dihydro- and 38·1% of tetrahydro-piperic acid were present, and the final result of the 50% hydrogenation, as calculated either from the proportion of unchanged acid or from the amount of dihydro-acids, is shown in Table II.

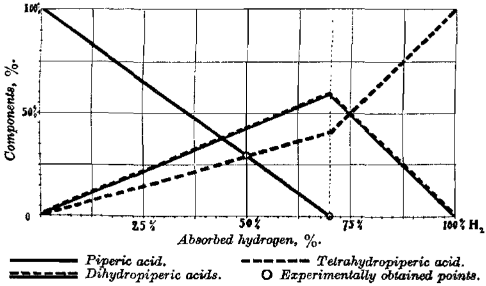
Table II.

Composition of 50% hydrogenation product (Paal's method).

	Calc. from amount of piperic acid.	Calc. from amount of dihydropiperic acids.	Mean.
Piperic acid	25%	27·6%	26·3%
Tetrahydropiperic acid......	25	27·6	26·3
Dihydropiperic acids	50	44·8	47·4
Total	100	100	100

The critical point of the hydrogenation, as determined graphically, is at 68% of hydrogen absorbed, and according to our views, all the piperic acid is exhausted at this point; Paal, however, states that it must be present at any moment of the process, and for, *e.g.*, 50% hydrogenation he postulates 50% of unchanged acid and 50% of tetrahydro-acid (contrast Table II). In order to settle this matter, we hydrogenated 2·4382 g. of piperic acid by Paal's method, allowing 447 c.c. (at 18° and 750 mm.) to be absorbed; since complete hydrogenation requires 541 c.c., the stage attained corresponds to 82·5% hydrogenation. The reaction product isolated dissolved completely in a small quantity of hot ligroin, which proves a total absence of piperic acid, and its m. p. was

FIG. 3.



89—93° (piperic acid has m. p. 216—217°). If the hydrogenation had proceeded as assumed by Paal, we should have found 17·5% of unchanged acid in the product.

Shapes of the Hydrogenation Curves.

In spite of the apparent total dissimilarity of the two curves in Fig. 1, they must both be related to the same type. Curve 2, according to the elements of its shape, is similar to the typical hydrogenation curves of conjugated systems of Type II (*e.g.*, the curves of di*iso*propenyl and piperylene): it differs only in the exceedingly sharp manifestation of its elements. The first section of the curve (prior to the critical point), corresponding to the hydrogenation of conjugated systems, has a clearly marked minimum. Such minima, often slightly marked, are to be found on the curves of conjugated systems of Type II (those for piperylene and its

mixtures being, however, more definitely marked). The minimum corresponds to the moment when the predominance of one kind of molecule gives way to that of another kind on the surface of the catalyst. This subject will be discussed in a future communication.

The second part of Curve 2, corresponding to a greater rate, is typical of most of the conjugated systems already studied (divinyl, isoprene, di*iso*propenyl, etc.). The third part represents the hydrogenation of the benzene ring.

Curve 1 differs from the other in that its second stage proceeds at a reduced rate instead of a higher one. This peculiarity might be attributed to the low rate of the process as well as to the thermal exchange with the surrounding medium, since we have often found that alteration in the conditions of the hydrogenation process, such as change of temperature, affects the shape of the curves. This question also will be dealt with later.

All our methods prove that the conjugated system is more rapidly exhausted under Paal's conditions than under our own; after the addition of 1 mol. of hydrogen, 26·3% of the piperic acid is unchanged in the former case and 34·3% in the latter. For this reason the position of the critical point is not the same, being at 68—70% and 75—76% in the two cases, respectively.

Summary.

(1) The hydrogenation of piperic acid in presence of platinum black, as well as in presence of colloidal palladium, proceeds according to Type II of our classification.

(2) The position of the critical point depends upon the catalyst chosen; in the former method, in alcoholic solution, it is at 75—76% of hydrogen absorbed, whereas in the latter it is at 68—70% if the potassium salt is used in aqueous solution.

(3) The hydrogenation curves obtained with either catalyst must be related to the same type, although they differ in shape.

MILITARY MEDICAL ACADEMY,
LENINGRAD. [*Received, November 12th*, 1928.]

XXXI.—*The Degradation of* l-*Arabinose.*

By VENANCIO DEULOFEU and RAÚL J. SELVA.

THE degradation of *l*-arabinose to erythrose, effected first by Wohl (*Ber.*, 1899, **32**, 3667) and Ruff (*Ber.*, 1901, **34**, 1365) and later by Weermann (*Rec. trav. chim.*, 1917, **37**, 16), has now been achieved by Zemplén's method (*Ber.*, 1926, **59**, 1254; 1927, **60**, 165), *viz.*,

XXXII.—*On Active Nitrogen. Part V* (Amended). *The Decay of the Nitrogen After-glow.*

By Eric John Baxter Willey.

The author regrets that an unfortunate error in the calculations upon his measurements of the decay of the nitrogen after-glow (J., 1928, 1620) has led to incorrect conclusions as to the process in question. It was previously stated that the reaction is of the fifth order, whereas it is now shown to be probably of the third, in agreement with the calculations made upon the life of the glow, a ternary decay process $2N + N_2 \longrightarrow 2N_2$ being assumed.

The experimental work is in no way affected.

Plotting the reciprocal of the square root of glow intensity against distance along the tube *D* (*loc. cit.*, p. 1621), *i.e.*, against time, so far as any one experiment is concerned, we obtain a linear relation as shown in Fig. 1 of the present paper. (The corresponding figure and legends in the earlier paper, Fig. 2, were incorrectly given, since the abscissæ represent $1/\sqrt{I}$ plotted with increasing values, and the ordinates represent *D* plotted with decreasing values, so the figure should be rotated through an angle of 90° in an anticlockwise direction; moreover, the descriptions of the first and last of the three curves should be interchanged.) The results must then be brought to a common basis for comparison, since the scale of time taken as proportional to distance along *D* will clearly alter for each change of pressure and gas flow rate as measured on the Venturi meter.

This must be done as follows: The "observed slope" gives $\frac{\Delta(1/\sqrt{I})}{\Delta\text{ (distance along tube)}}$, whilst the "corrected slope" is desired to give $\Delta(1/\sqrt{I})/\Delta t$, whence $\frac{\text{(corrected slope)}}{\text{(observed slope)}} = \frac{\Delta\text{ (distance along tube)}}{\Delta t}$ which varies as $\frac{\text{(flow rate at } N.T.P.)}{\text{(gas pressure)}}$.

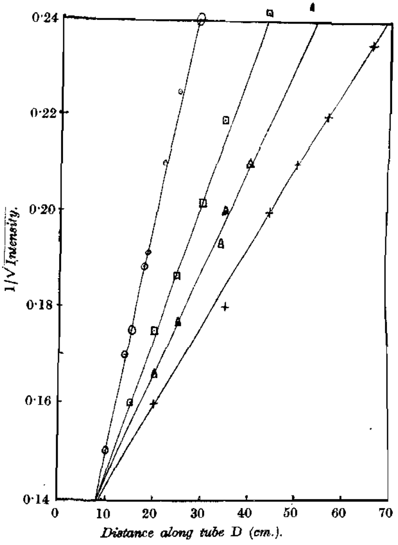
Hence the "corrected slope" $= \frac{\text{"observed slope"} \times \text{flow rate}}{\text{gas pressure}}$.

In the previous paper the error was made of multiplying the observed slopes by $\frac{\text{gas pressure}}{\text{flow rate}}$ instead of applying this correction to distances measured along the observation tube *D*; in this way the *inverse* of the true factor was employed.

The author has accordingly replotted his experimental data, using

the correct factor for reducing them to a common basis, and the plot of corrected slopes against gas pressure is given in Fig. 2. It appears now that the slopes of the $1/\sqrt{I},t$ plot vary as the total gas pressure p.

Fig. 1.



Flow rate of 2200 *c.c./hr. at* N.T.P. *in all cases.*

+ = 4·0 *mm. pressure.* ⊡ = 6·2 *mm. pressure.*
△ = 5·3 „ „ ⊙ = 7·0 „ „

All curves pass through the same point on the axis of distance for $1/\sqrt{I}=0{\cdot}14$.

The interpretation of this is not clear. Assuming that the emission of the glow occurs through a ternary collision $2N + N_2 \rightarrow 2N_2$, we may show that the slope of the $1\sqrt{I},t$ plot should vary as $\sqrt{p}$ as follows: Let the concentration of atoms per c.c. at any instant be n and that of the molecules N: A, B, and C are constants.

Then $-\frac{d\nu}{dt} = A\nu^2 N$, whence $\nu = \frac{1}{AN} \cdot \frac{1}{t+B}$, and I will thus be given by $I = C\nu^2 N$. Hence

$$\frac{1}{\sqrt{I}} = \frac{1}{\sqrt{CN}} \cdot \frac{1}{\nu} = \frac{A}{\sqrt{C}} \cdot \sqrt{N} \cdot (t + B);$$

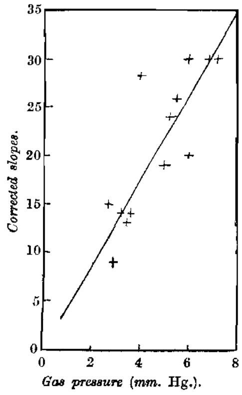
and therefore the slope of the $1/\sqrt{I},t$ plot will vary as the square root of the gas pressure.

It follows then that, although these results show the calculations on p. 1625 of the earlier paper to be approximately supported, the measurements indicate that the reaction proceeds in a manner other than would be the case were it truly of the third order; for a ternary decay we should have $d\nu/dt = K_1[N]^2[N_2]$, whereas these experiments give

$$d\nu/dt = K_2[N]^2[N_2]^2,$$

since the value of K_1 varies as $[N_2]$.

FIG. 2.



In view of the limited range of pressures over which these experiments extend, it does not appear safe to attempt a further explanation of the results, but they are rather suggestive of a reaction having taken place on the surface as well as in the gas phase; it has repeatedly been noticed by the author that the life of the after-glow is dependent to a large extent upon the nature of the containing vessel, being as a rule much longer in Pyrex glass than in the soda glass used in these experiments, although the cleaning process was the same in both cases. Moreover, Herzberg (*Z. Physik*, 1928, **46**, 878) has shown that surface phenomena probably play a great part in the reactions which lead to the production of the after-glow.

The author is indebted to Dr. H. O. Kneser (private communication) for the information that his recent measurements tend to show that the decay of the after-glow is truly of the third order under his experimental conditions, and it is possible that the discrepancy between our results is to be found here.

Further emendations in the earlier paper are that paragraph (*a*), p. 1626, must be deleted, and (*e*), p. 1627, amended to the statement

that, unless the impact of the neutral molecule upon the excited body first formed from the atoms occurs within the life of the latter, the energy of recombination may be lost by radiation, leading to an anticipation that the decay mechanism will alter at low pressures together with the chemical and physical attributes of the active nitrogen, as discussed. Equations (2) and (3) on p. 1627 must also be omitted.

It may finally be stated that references to $\sqrt{I}$ in the earlier paper should clearly be to $1\sqrt{I}$, since from equation (2) on p. 1625 we have

$$d\nu/dt = K\nu^2, \text{ i.e., } -1/\nu = Kt + c,$$

hence

$$\sqrt{I} = \sqrt{\frac{K\nu^2}{k}} = -\frac{1}{Kt+c}\sqrt{\frac{K}{k}}$$

(where c is an integration constant), and hence $\sqrt{I}$ cannot possibly show a linear relation with time. The plot of $1/\sqrt{I}$ against time has, in fact, always been employed.

The author is much indebted to Mr. B. Topley for pointing out these errors.

Summary.

It is shown that, owing to an arithmetical error in an earlier communication (J., 1928, 1620), the conclusion that the decay process of the nitrogen after-glow is of the fifth order is incorrect, and that it is rather probably of the third order, but complicated by a surface reaction taking place at the same time as that in the bulk of the gas. The conclusions as to the chemically active nitrogen probably being formed during the degradation of energy from a high-level molecule initially formed from atoms through the medium of a ternary collision $2N + N_2 \longrightarrow 2N_2$ remain unaltered, as do other considerations upon the behaviour of active nitrogen.

93, Cromwell Road,
Northwich, Cheshire.

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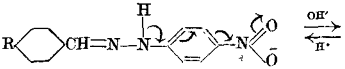
XXXIII.—*Colour and Constitution. Part IV. The Absorption Spectra of Nitrophenylhydrazones in Alcohol and in Alcoholic Potassium Hydroxide.*

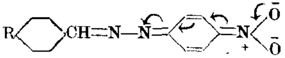
By Herbert Henry Hodgson and Kenneth Ernest Cooper.

The presence of a nitro-group in the ortho- or para-position in a phenylhydrazone induces incipient ionisation of the imino-hydrogen. That the treatment of such hydrazones with hydroxyl ions renders the ionisation actual, with the consequent formation of a quinonoid

structure, was suggested by Chattaway and Clemo (J., 1923, **123**, 3041) to explain the resulting intense colorations, and their view is supported by the fact that no such colours are produced in the absence of either the imino-hydrogen or the *o*- or *p*-nitro-group.



(I, yellow.)



(II, magenta.)

It has been suggested (*Brit. Assoc. Reports*, 1922, 298) that the combination of two atoms involving a loss of energy ε results in a compound capable of absorbing light of frequency $\varepsilon = h\nu$. We suspected that the colour of the ions represented by formula (II) might bear a relation to the energy changes involved in the ionisation of the imino-hydrogen by the action of the hydroxyl ions. The greater the initial degree of incipient ionisation, the less will be the energy required for the ionisation and the lower, it is presumed, will be the frequency of the radiation absorbed by the ion. The present investigation records the influence of a series of substituents (R in I) whose effects upon the ease of ionisation are known. The combined direct and inductive effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401; Cooper and Ingold, J., 1927, 836; Ingold and Vass, J., 1928, 417) places the groups in the following order.*

R = O(−), CH_3, NMe_2, OMe, Cl, (+)NMe_3{$\overset{(-)}{OH}$

← Inhibiting ionisation. Enhancing ionisation. →

The results (Fig. 1) are in agreement with the above series, and although the differences are small, as would be expected from the distance these effects have to travel, they are definite.

p-Substituted benzaldehyde-*p*-nitrophenylhydrazones in alcoholic KOH.

R	(+)NMe_3{$\overset{-}{O}H$	Cl	OMe	NMe_2	CH_3	O(−)
Head of band...	580	565	550	545	542	530
Curve (Fig. 1)	I	II	III	IV	V	VI

The order of the absorption curves of the hydrazones without the addition of alkali is, on the other hand, entirely different (Fig. 2). It is significant that the maximum looseness of the electronic

* The tautomeric effect of these groups will have little or no influence, for in the process of ionisation no demand is made for a negative charge (compare the ionisation constants of substituted acids; Ingold and Shaw, J., 1927, 2923).

structure produced by the introduction of the NMe_2 group, with its mobile unshared electrons, is accompanied by the maximum wave-length, and the maximum tightening of the system by the $(+)NMe_3$ with the minimum wave-length. This is in agreement with the known effects of salt formation on the absorption of aniline and phenol (Baly and Collie, J., 1915, **107**, 1338).

p-Substituted benzaldehyde-*p*-nitrophenylhydrazones in alcohol.

R	NMe_2	OH and OMe	Cl	CH_3	$(+)NMe_3Cl(-)$
Head of band	460	415	400	400	395
Curve (Fig. 2)	IV	VI and III	II	V	I

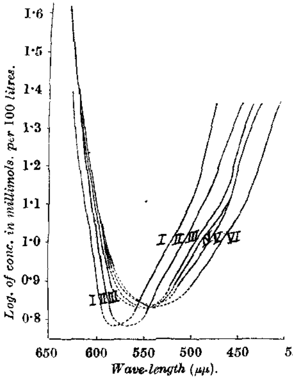


FIG. 1.

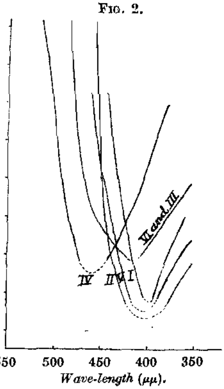


FIG. 2.

The order of the effect of substituents in this series, *viz.*, $NMe_2 > OMe > Cl = CH_3 > +NMe_3$, is in accordance with the well-known bathochromic effect of the amino- and the hydroxyl group as compared with the uncertain effects of chlorine in the dyes.

The nitrophenylhydrazones were chosen in preference to the nitrobenzaldehydephenylhydrazones because they require much less alkali to effect complete ionisation and produce their characteristic colours (Hodgson and Beard, J., 1927, 2382). That the absorption band is characteristic of the ion will be shown in a future paper (private communication from Mr. Handley).

EXPERIMENTAL.

Benzaldehyde-p-trimethylammonium iodide, prepared by refluxing a slight excess of methyl iodide with *p*-dimethylaminobenzaldehyde

for 6 hours, crystallised from water in colourless plates, m. p. 152° (Found: I, 43·8. $C_{10}H_{14}ONI$ requires I, 43·6%).

Benzaldehyde-p-*trimethylammonium chloride* p-*nitrophenylhydrazone* was obtained by warming theoretical quantities of the two components in acetic acid for 10 minutes and diluting the solution with water (5 vols.); after recrystallising from hydrochloric acid and then from alcohol, it melted at 196° (Found: Cl, 10·9. $C_{16}H_{19}O_2N_4Cl$ requires Cl, 10·6%).

p-*Hydroxybenzaldehyde*-p-*nitrophenylhydrazone*, recrystallised from alcohol, had m. p. 262° (Found: N, 16·5. $C_{13}H_{11}O_3N_3$ requires N, 16·3%).

Absorption spectra were photographed with an iron arc through 1 cm. thickness of solutions of concentration $2M/10,000$, $2M/15,000$, $2M/20,000$, and $2M/25,000$ and of intermediate concentrations when necessary. The concentration of alkali for the curves in Fig. 1 was approximately 200 mols. of potassium hydroxide per mol. of hydrazone, largely in excess of that required to produce the desired band and destroy the band of the hydrazone. All solutions were kept in well-stoppered bottles, since they easily oxidised in the air in the presence of alkali.

We wish to record our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us (K.E.C.) to take part in this research, and to Prof. C. K. Ingold, F.R.S., and Prof. E. C. C. Baly, F.R.S., for the very kind interest they have shown in this work.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 13th, 1928.*]

XXXIV.—*An X-Ray Examination of some Salts of the Fatty Acids.*

By STEPHEN HARVEY PIPER.

X-RAY photographs were taken with the $K\alpha$ rays of copper or iron reflected from thin layers of the salts pressed on a glass strip and mounted on a Müller spectrograph. The salts were in the form of thin flakes, and this method is convenient for obtaining the reflexions from the widely spaced crystal planes parallel to the flake surface. Salts of long-chain compounds of this type crystallise with these planes separated by the lengths of two molecules placed end to end with like groups in contact, and the axis of the chain is usually tilted with respect to the plane. The spacing measured, *i.e.*, the perpendicular distance between the planes, may be conveniently spoken of as twice the *effective* length of the molecule.

Many of the salts, being very deliquescent, were kept in a desiccator provided with windows and maintained at a temperature of 80° during the exposure. The windows were covered with a thin semi-transparent animal membrane prepared by the Badische Fabrik for covering scent-bottle stoppers; as this has no appreciable absorption for X-rays, is impermeable to moisture, and is unaffected at 100°, it is very suitable for the purpose.

The existence of two types of potassium salts was first noticed when a second and larger spacing appeared on the photograph of a specimen of the stearate which had been exposed to the atmosphere for some days. It seemed possible that this spacing was due to the presence of an acid * salt, and preparation of the acid salt immediately confirmed this hypothesis, the photograph showing only the large spacing. Dr. T. Malkin kindly undertook the preparation of several of these acid salts,† and I wish to express my gratitude to him for supplying these and most of the normal salts. It is sufficient to state here that the normal salts and acid salts containing eight or more carbon atoms separate on cooling from a warm alcoholic solution to which has been added the *theoretical* amount of alcoholic caustic potash. Those of less than eight carbon atoms separate on evaporation of the alcoholic solution.

Pure salts give brilliant photographs on which it is possible to measure the orders of reflexion right across the plate, so that an accuracy of 1% is easily obtained, and this may be regarded as the maximum probable error in the individual spacings now given. Traces of impurity give rise to small distorted crystals, the reflexions give few orders and broad ill-defined lines, and the spacings usually differ from those of the pure salt.

The type of reflexion resembles that first obtained by Müller for the fatty acids (J., 1923, **123**, 2043), *i.e.*, strong odd orders and weaker even orders. This effect (see Shearer, *Proc. Roy. Soc.*, 1925, *A*, **108**, 655) is due to the weak reflexions from the planes containing the light methyl groups being in opposite phase to the strong re-

* Theoretically, of course, an acid salt of a monobasic fatty acid cannot exist. In conformity with other workers, however, we use the term to imply an equimolecular compound of the free acid and the neutral salt.

† The acids used in this work are of the highest degree of purity. Lauric, myristic, palmitic, stearic, and behenic acids were purified by careful fractional distillation of the ethyl esters (compare Piper, Malkin, and Austin, J., 1926, 2312, footnote). With the exception of pentadecoic acid, which was kindly provided by Professor Garner, the acids were obtained by nitrile and malonic ester syntheses, an account of which will be published later. Throughout the latter work, the physical data for intermediates and acids were found to correspond closely with those given by Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905), which may be regarded as criteria of a high degree of purity.

flexions from the planes containing the heavier active groups. *Since active groups containing potassium atoms have a higher* scattering power than carboxyl groups, the interference of the reflexions from the CH_3 planes is not so marked as with the acids, and the even orders are stronger. The weakening of the even-order reflexions is slightly more marked in the acid than in the normal salts, as would be expected, for here presumably one hydrogen and one potassium atom take the place of two potassium atoms in the planes which contain the active groups.

In contrast with the acids, which possess a number of crystalline forms (Piper, Malkin, and Austin, J., 1926, 2310; de Boer, *Nature*, 1927, **119**, 634), only one form appears to exist for these pure anhydrous salts at the ordinary temperature. For this reason they are very well suited for *X*-ray measurements for analytical purposes. The spacings are shown in Table I. Previous measurements on salts of fatty acids are those of Piper and Grindley (*Proc. Physical Soc.*, 1923, **35**, 269) and Trillat (*Compt. rend.*, 1925, **180**, 1838).

TABLE I.

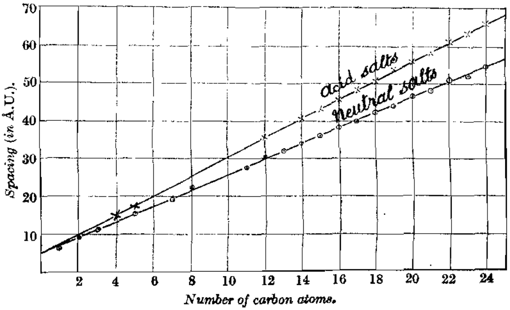
Salt.	No. of C atoms.	Spacing, in Å.U. Normal salt.	Spacing, in Å.U. Acid salt.	Salt.	No. of C atoms.	Spacing, in Å.U. Normal salt.	Spacing, in Å.U. Acid salt.
Formate	1	6·4	—	Pentadecoate	15	35·8	42·90
Acetate	2	9·13	—	Palmitate	16	37·9	45·29
Propionate ...	3	11·4	—	Margarate ...	17	39·77	48·10
Butyrate ...	4	—	14·90	Stearate	18	42	50·47
Valerate	5	15·55	17·07	Nonadecoate	19	43·8	53·03
Heptoate ...	7	19·16	—	Eicosoate	20	46·45	55·65
Octoate	8	22·3	—	Heneicosoate	21	47·85	58·35
Undecoate ...	11	27·45	—	Behenate	22	50·72	60·78
Laurate	12	30·2	35·53	Tricosoate......	23	51·8	63·25
Tridecoate ...	13	31·85	—	Lignocerate ...	24	54·45	65·94
Myristate ...	14	33·95	40·45				

The spacings are plotted against the number of carbon atoms in the chain in Fig. 1. It appears that, with the exception of potassium formate, the odd and even neutral salts lie on a straight line with an origin at 5 Å.U. The acid salts lie on another straight line starting from the same origin, and the slope of each of these lines gives the *effective* length of two CH_2 groups in the particular type of chain concerned.

The accepted diameter of the carbon atom is 1·54 Å.; and the maximum possible value of the effective length of the CH_2 group, if the lines joining the centre of two successive carbon atoms are inclined at the tetrahedral angle of 109° 28′, is 1·257 Å. (Müller and Shearer, J., 1923, **123**, 3159). I find that the effective length is

1·03 Å. in the normal salts, and 1·275 Å. in the acid salts. The smaller effective length for the normal salts might be explained by assuming that the tetrahedral angle exists in the chain and that the whole chain is inclined at 54° 54′ to the axis. The effective length of 1·275 Å. is slightly too great to be explained on the basis of a tetrahedral angle in the chain; if we assume that the chain is oriented perpendicularly to the reflecting planes, the angle would be 111° 46′, but there is no independent evidence for assuming that the chain is perpendicular. If the chain were tilted, the angle would have to exceed the tetrahedral angle by a still larger amount. Another alternative is that the diameter of the carbon atom is 1·56 Å. instead of 1·54 Å., the chain being perpendicular and the

Fig. 1.



angle tetrahedral, but it is not likely that the diameter of the carbon atom is variable. The choice between these alternatives can only be decided by a complete analysis of single crystals.

Müller (*Proc. Roy. Soc.*, 1928, *A*, **120**, 437) concludes that the chain of a normal hydrocarbon is a flat zig-zag in which the tetrahedral angle is conserved within ½%, and it is, therefore, important to decide whether the variation found for these salts is within the limits of experimental error.

The value of 1·275 exceeds the above value of 1·257 by 1·4%; no single spacing has a maximum error of more than ±1%, and most are correct to ±0·5%. In Table II the values of $\Delta s/\Delta n$, the spacing increase per carbon atom, are calculated for eight pairs of values. It will be noticed that all values of $\Delta s/\Delta n$ are greater than 1·257, and only one differs from the mean by as much as 1%. Since an

TABLE II.

No. of C atoms.	Spacing.	Diff.	$\Delta s/\Delta n$.	Difference from mean.	% Variation from mean.
24 17	65·94 48·10	17·84	1·275	0	0
23 16	63·25 45·29	17·96	1·283	+0·008	+0·6
22 15	60·78 42·90	17·88	1·277	+0·002	+0·15
21 14	58·35 40·45	17·90	1·278	+0·003	+0·23
20 12	55·65 35·53	20·12	1·259	−0·016	−1·30
19 5	53·03 17·07	35·96	1·284	+0·009	+0·7
18 4	50·47 14·90	35·57	1·271	−0·004	−0·3
			Mean 1·275		

impurity can alter the spacing, it is possible that the large variation from the mean in this case is due to contamination of one of the salts. The mean value of $\Delta s/\Delta n$ is identical with that measured from the graph.

It appears, therefore, that the difference from the tetrahedral chain is real, and that the chain in these salts differs from the hydrocarbon chain, possibly owing to attractions between the active end groups. The divergence of the s–n graph from the line drawn from the same origin for a tetrahedrally spaced chain is quite noticeable when plotted on a large scale, and on the same scale there appears a tendency for the odd-numbered *normal* salts to lie below the even-numbered, although the variations in this case are nearer the possible experimental errors.

Dr. Malkin has also prepared some acid sodium salts. In contrast to the normal sodium salts, these crystallise beautifully, and the spacings obtained are given below. It is noticeable that all three have larger spacings than the corresponding potassium salts, a rather surprising result in view of the smaller size of the sodium atom. The spacings of two normal thallium salts (very kindly given me by Dr. Menzies) are included to bring out the very small change in the spacing that is produced by the addition of a very heavy metallic atom.

TABLE III.

Salt.	No. of C atoms.	Spacing, in A.U.
Acid sodium laurate	12	35·76
Acid sodium palmitate	16	46·05
Acid sodium stearate	18	50·6
Thallium palmitate	16	38·8
Thallium stearate	18	42·2

Gibbs (J., 1924, **125**, 2622) concludes that a linear relationship of this nature does not exist for the lower members of the fatty acids. It is hoped to show in a further communication that this apparent breakdown of the linear law can, in part at least, be attributed to multiplicity of crystalline form.

Summary.

X-Ray photographs show that the potassium salts of the fatty acids have spacings increasing uniformly with the carbon content from 2 to 24 atoms. Another similar series of spacings exists for acid salts, *i.e.*, equimolecular compounds of free acid and neutral salt. The chain in this type of salt cannot be accounted for by a tetrahedral angle of 109° 28′ between the lines joining the centres of successive atoms—at least 111° 46′ is required.

I am indebted to Mr. T. Howard and Mr. Leacy for taking some of the photographs. Part of the expenses of the work were covered by a grant from the University Colston Research Society.

THE H. H. WILLS PHYSICAL LABORATORY,
THE UNIVERSITY, BRISTOL. [*Received, September 14th*, 1928.]

XXXV.—*The Influence of the Polarity of the Solvent on the Velocity of a Reaction.*

By ROBERT NAPIER KERR.

THE purpose of this investigation was to examine the relationship between the influence which a solvent exerts on the velocity of a reaction and the polar properties of that solvent as measured by the electric moment of the molecule. For this purpose it was necessary to select solvents having similar constitutions but considerably different electric moments, and accordingly certain isomeric disubstituted benzene derivatives were chosen. The reaction between allyl bromide and pyridine appeared to be suitable for the study, since Hawkins (J., 1922, **121**, 1170) had already found for this reaction an approximate connexion between the influence of the solvent and the dielectric constant.

EXPERIMENTAL.

Satisfactory results were not obtained by the method given by Hawkins, and ultimately the following procedure was adopted. Solutions of pyridine (approx. 2*M*) and of allyl bromide (approx. *M*) in the required solvent were prepared, and 2 c.c. of each were transferred by a calibrated pipette to a bulbed tube, which was

rapidly sealed and placed in a thermostat, the time of insertion being taken as zero time for the reaction. After a definite interval the reaction was stopped by pouring the mixture into dilute nitric acid. The unchanged allyl bromide was removed by shaking with benzene, and the amount of quaternary compound formed was then determined by Volhard's thiocyanate method. The velocity coefficients were calculated from the equation $k = 1/t(a-b) \cdot \log_e b(a-x)/a(b-x)$; four or five determinations were carried out for each isomeride and the coefficients obtained were reasonably constant in all cases. Two examples of the results obtained are given below; a, b, and x (in g.-mols./l.) are respectively the initial concentrations of pyridine and allyl bromide and the concentration of the quaternary compound formed in time t (in minutes).

Solvent: benzene. $a = 0{\cdot}979$; $b = 0{\cdot}496$.

t.	x.	$k \times 10^6$.
113	0·1331	304
158	0·1731	308
210	0·2109	308
257	0·2432	313
334	0·2788	305

Solvent: *m*-tolyl methyl ether. $a = 0{\cdot}983$; $b = 0{\cdot}498$.

t.	x.	$k \times 10^5$.
26	0·1174	1122
34	0·1416	1102
41	0·1656	1105
48·5	0·1871	1102

A modified procedure was employed with solvents which were solid at room temperature and also where the amount of material available was small. Some of the solid was weighed into a tube and the calculated weight of pyridine was then added. The tube was placed in the thermostat and after the contents had melted the calculated volume of allyl bromide was added from a 1 c.c. graduated pipette. The contents of the tube were removed for analysis by washing out with hot benzene. For the calculation of the velocity coefficient, the volume of the solution was taken as the sum of the volumes of the solvent and of the two reactants. This method of procedure was not as accurate as the first, but a larger number of determinations were made and the average taken; thus, with *p*-nitrotoluene, $100k = 629$, 603, 589, 619, 628, 618.

All the solvents used, with the exception of *m*-dichlorobenzene, were B.D.H. reagents; the liquids were carefully fractionated and the solids recrystallised from alcohol. The *m*-dichlorobenzene was a sample from a previous research, and as only a small quantity was available it was not redistilled before use. Both the pyridine (b. p. 116·8° after refluxing over caustic potash) and the allyl bromide (b. p. 69·8—70·0°) were kept in the dark and remained colourless throughout the experiments.

The results are summarised in Table I. The velocities of reaction in the corresponding monosubstituted derivatives as solvents have also been determined under the same conditions, and are included

for comparison. In the second column are given the ranges of x for which the reaction has been investigated, in the third the extent of variation of k obtained, in the fourth the average value of k, and in the last there are reproduced the figures for the electric moment, μ, found by Smyth and Morgan (*J. Amer. Chem. Soc.*, 1928, **50**, 1544) and Williams and Schwingel (*ibid.*, p. 366). All experiments were carried out at 56·4° ± 0·1°.

TABLE I.

Solvent.	x.	$k \times 10^2$ (range).	$k \times 10^2$ (mean).	$\mu \times 10^{18}$.
Benzene	0·133—0·279	0·304—0·313	0·308	0·20
Chlorobenzene	0·106—0·255	0·917—0·940	0·924	1·56
o-Dichlorobenzene	0·119—0·201	1·533—1·588	1·566	2·25
m- ,, ,,	0·102—0·143	0·847—0·886	0·866	1·48
p- ,, ,,	0·131—0·171	0·792—0·812	0·799	0·00
Anisole	0·168—0·268	1·545—1·605	1·581	
o-Tolyl methyl ether	0·082—0·190	0·822—0·835	0·829	
m- ,, ,,	0·117—0·187	1·102—1·122	1·108	
p- ,, ,,	0·115—0·190	1·087—1·120	1·103	
Nitrobenzene	0·355—0·395	9·70—10·52	10·15	3·90
o-Nitrotoluene	0·313—0·432	5·902—6·100	5·993	3·75
m- ,,	0·297—0·371	4·646—4·872	4·841	4·20
p- ,,	0·322—0·431	5·891—6·290	6·145	4·50

Discussion of Results.

Consideration of the above results shows that in certain cases the marked differences found in velocity in the isomerides can be explained by the size of the moment of the molecule. For instance, *m*-dichlorobenzene has approximately the same moment as chlorobenzene and the rate in the two solvents is nearly equal; on the other hand, the *o*-isomeride has a greater moment and the velocity is correspondingly increased. Although no values for the moments of the tolyl methyl ethers are yet available, the dielectric constants as determined by Philip and Haynes (J., 1905, **87**, 1000), *viz.*, *o*- = 3·57, *m*- = 4·08, *p*- = 4·03, show that the velocities in these isomeric solvents are also in striking accord with their polar nature. In other cases, however, variations occur in the velocity which would not be expected from the moments; *e.g.*, *p*-dichlorobenzene has zero moment which leads one to predict a velocity in it comparable with that in benzene, whereas actually the value found is more than twice as great. Similarly there is no evidence from the moments of the molecules to account for the rate in *m*-nitrotoluene being markedly lower than in its two isomerides.

The conclusion may be drawn, therefore, for these isomerides that in some cases the influence of the solvents can be connected satisfactorily with the moments of their molecules, but that in other cases

differences of velocity occur which are not due to changes in the molecular moments.

The author wishes to thank Prof. J. F. Spencer for his interest in this work and also the Research Fund Committee of the Chemical Society for a grant in aid of it.

BEDFORD COLLEGE (UNIVERSITY OF LONDON),
REGENT'S PARK, N.W. 1. [*Received, November 24th*, 1928.]

XXXVI.—*The Preparation of Some Metallic Chromates.*

By SAMUEL HENRY CLIFFORD BRIGGS.

THE normal chromates of copper, zinc, and cadmium were first obtained by Schulze (*Z. anorg. Chem.*, 1895, **10**, 148) in an insoluble anhydrous form by heating solutions of the dichromates with the corresponding hydroxides in sealed tubes. The author has confirmed these results and also prepared the normal chromates of nickel and cobalt (*ibid.*, 1908, **56**, 246; 1909, **63**, 325). Britton (J., 1926, 134) studied the precipitation of basic zinc chromate and, apparently without attempting to repeat Schulze's experiments, made the following statement: "An insoluble normal zinc chromate has been stated to exist by Schulze and by Briggs, but the latter's data are unconvincing." In view of this criticism the previous work has been repeated, and the existence of the normal zinc chromate described by Schulze has once more been confirmed.

During attempts to obtain other normal chromates by various modifications of Schulze's method, the following crystalline *compounds* were prepared: $9ZrO_2,5CrO_3,12H_2O$; $3Al_2O_3,2CrO_3,6H_2O$; $2Fe_2O_3,4CrO_3,H_2O$; $3SbO_2,2CrO_3$; and also the chromites $2Sb_2O_3,Cr_2O_3$ and $3Bi_2O_3,2Cr_2O_3$. With the exception of the complex iron compounds of Hensgen (*Ber.*, 1879, **12**, 1300), no definitely crystalline chromates of aluminium, iron, or antimony appear to have been previously described.

The normal chromates of copper, cadmium, and cobalt have also been obtained in an insoluble hydrated form by the action of sodium chromate on a large excess of highly concentrated solutions of the corresponding dichromates. The normal chromates of nickel and zinc could not be prepared by this method, in accordance with Britton's observations on zinc chromate (*loc. cit.*).

EXPERIMENTAL.

Zinc Chromate.—By an alteration in the proportions of the reagents the normal chromate of zinc was obtained free from the

basic salt present in the earlier preparations. Chromium trioxide (5 g.) was mixed with 4·5 g. of zinc carbonate (ZnO, 70%) and 5 c.c. of water in a glass tube, and the mixture warmed until evolution of carbon dioxide ceased. The tube was then sealed and heated for 4 hours at 200—210°. After being washed with cold water and dried, the product was a yellow, satiny powder (Found: ZnO, 45·4; CrO_3, 54·7. Calc.: ZnO, 44·9; CrO_3, 55·1%). Under the microscope it appeared homogeneous and consisted of a felted mass of acicular crystals. It was sufficiently soluble in water to give a distinctly yellow solution.

Zirconium Chromate, $9ZrO_2,5CrO_3,12H_2O$.—Crystallised zirconium nitrate (7 g.) in 50 c.c. of water was added to 10 g. of potassium dichromate in 80 c.c. of water. The precipitate was filtered off after 1 day, washed with a little water, and dried in a vacuum. The dried, powdered product (2·5 g.) was heated in a sealed tube for 3½ hours with 6 g. of chromium trioxide and 6 c.c. of water at 190°. An orange-red, homogeneous, crystalline powder was obtained, which was insoluble in water (Found: ZrO_2, 60·7; CrO_3, 27·0; ZrO_2 + Cr_2O_3, 81·2. $9ZrO_2,5CrO_3,12H_2O$ requires ZrO_2, 60·7; CrO_3, 27·4; ZrO_2 + Cr_2O_3, 81·6%).

Aluminium Chromate, $3Al_2O_3,2CrO_3,6H_2O$.—4 G. of hydrated aluminium chloride in 25 c.c. of water were added to a solution of 15 g. of sodium chromate in 30 c.c. of water, and the mixture was heated for 1 hour on the water-bath. The filtered precipitate was washed with a little water and dried in a vacuum. The finely powdered product (1·8 g.) was heated in a sealed tube for 4 hours at 200—210° with 2 g. of chromium trioxide and 2 c.c. of water. A crystalline, insoluble, lemon-yellow powder was obtained (Found: Al_2O_3, 49·6; CrO_3, 32·3. $3Al_2O_3,2CrO_3,6H_2O$ requires Al_2O_3, 49·8; CrO_3, 32·6%).

Ferric Chromate, $2Fe_2O_3,4CrO_3,H_2O$.—This *compound* was prepared from 5 g. of ferric chloride, the procedure and the quantities of the other reagents being exactly the same as with the aluminium salt; it was a brownish-black, insoluble solid (Found: Fe_2O_3, 43·7; CrO_3, 53·7. $2Fe_2O_3,4CrO_3,H_2O$ requires Fe_2O_3, 43·3; CrO_3, 54·2%). Under the microscope it was seen to consist of shining, black crystals mixed with a trace of a lighter-coloured substance, evidently of a more basic character as shown by the analysis. The formula may also be written $2(FeCrO_4)_2O,H_2O$, and the compound is therefore analogous to the dichromate $(FeCr_2O_7)_2O$ described by Calcagni (*Gazzetta*, 1925, **55**, 396).

Antimony Chromate, $3SbO_2,2CrO_3$.—Antimony oxychloride, $2SbOCl,Sb_2O_3$ (3·5 g.), was heated for 4 hours in a sealed tube at 200° with 6 g. of chromium trioxide and 6 c.c. of water. On

opening the tube, a trace of a straw-coloured sublimate was observed, probably an oxychloride, and an orange-coloured deposit present in the liquid was found to consist of crystalline, spherical aggregates, insoluble in water but slowly soluble in nitric acid. The *compound* was analysed by decomposition with concentrated sulphuric acid, followed by digestion on the water-bath with a solution of tartaric acid until it was completely dissolved. The antimony was precipitated with hydrogen sulphide, and the filtrate evaporated and ignited, leaving the chromium as sesquioxide (Found : SbO_2, 69·53 ; CrO_3, 30·52. $3SbO_2,2CrO_3$ requires SbO_2, 69·76 ; CrO_3, 30·24%). Several attempts to repeat the preparation of this compound failed, the following chromite being obtained. It is proposed to make a further investigation of the chromates of antimony.

Antimony Chromite, $2Sb_2O_3,Cr_2O_3$.—The oxychloride $2SbOCl,Sb_2O_3$ (3·5 g.) was heated as before for 5 hours at 200° with 8 g. of chromium trioxide and 8 c.c. of water. The chromic acid was partly reduced, and there was formed a brown powder mixed with a dark-coloured liquid which had a strong odour of chlorine. The solid, after being thoroughly washed and dried, had the appearance of powdered stone (Found : Sb_2O_3, 80·0 ; CrO_3, 19·9. $2Sb_2O_3,Cr_2O_3$ requires Sb_2O_3, 79·3 ; CrO_3, 20·7%). It was totally insoluble in alkalis, water, or acids, including aqua regia.

Bismuth Chromite, $3Bi_2O_3,2Cr_2O_3$.—This was prepared (5 g. BiOCl ; 6 g. CrO_3 ; 6 c.c. water) in the same way as the antimony chromite, which it resembled in appearance and properties (Found : Bi_2O_3, 82·7 ; Cr_2O_3, 18·0. $3Bi_2O_3,2Cr_2O_3$ requires Bi_2O_3, 82·1 ; CrO_3, 17·9%).

An attempt was made to prepare a normal chromate from bismuthyl dichromate by a similar method, but only unchanged material was recovered.

Copper Chromate, $CuCrO_4,2H_2O$.—A solution of 4·5 g. of crystallised sodium chromate (73% Na_2CrO_4) in 20 c.c. of water was added in the cold to a solution of 17 g. of copper carbonate in 30 c.c. of water containing 30 g. of chromium trioxide. The reddish-brown precipitate was filtered off and washed with cold water. It weighed 2 g. and under the microscope it was seen to be crystalline and homogeneous (Found : Cu, 29·7 ; CrO_3, 46·6. Calc. : Cu, 29·5 ; CrO_3, 46·4%).

Cobalt Chromate, $CoCrO_4,2H_2O$.—This was prepared in exactly the same way as the copper compound, and obtained as a black, microcrystalline powder (Found : Co, 28·1 ; CrO_3, 47·4. Calc. : Co, 27·9 ; CrO_3, 47·4%).

Cadmium Chromate, $CdCrO_4,H_2O$.—This was prepared in the

same way and consisted of a bright yellow, crystalline powder (Found : Cd, 45·3 ; CrO_3, 40·9. Calc. : Cd, 45·6 ; CrO_3, 40·6%).

The water molecules in the normal chromates of copper, cobalt, and cadmium are very firmly attached and are not evolved in a vacuum over sulphuric acid.

Nickel Chromates.—When an attempt was made to prepare a normal chromate of nickel in the same way as for copper, a clear solution was obtained, from which at the summer temperature a deep red compound crystallised very slowly, 1·9 g. having separated after 4 days. The red *compound* appeared homogeneous under the microscope, but had a very complex constitution [Found : Ni, 25·9 ; CrO_3, 49·7 ; loss, after twelve days in a vacuum over sulphuric acid, 4·1 ; Na, 5·2. $2Na_2CrO_4,7NiCrO_4,Ni(OH)_2,10H_2O$ requires Ni, 25·8 ; CrO_3, 49·5 ; $4H_2O$, 4·0 ; Na, 5·1%].

In another experiment a solution of 40 g. of chromium trioxide in 40 c.c. of water was saturated with nickel carbonate ; 15 g. of sodium chromato in 25 c.c. of water were then added with vigorous stirring and the mixture was cooled to 0°. In spite of inoculation with nickel sulphate and magnesium chromate, no crystals of normal nickel chromate separated, but a slight brown deposit having approximately the composition $2NiO,CrO_3,5H_2O$ had formed after 2 hours (Found : Ni, 34·9 ; CrO_3, 28·9 ; $3H_2O$, loss after five months over sulphuric acid in a vacuum, 15·9. Calc. : Ni, 34·6 ; CrO_3, 29·4 ; $3H_2O$, 15·9%).

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XXXVII.—*The Inflammation of Mixtures of the Olefins and Air in a Closed Spherical Vessel.*

By George Barton Maxwell and Richard Vernon Wheeler.

Parallel experiments to those already described (J., 1927, 2069) on the inflammation of mixtures of the paraffins and air have been made with ethylene, propylene, and butylene. The mixtures, initially at atmospheric pressure and room temperature (about 17°), were ignited by a secondary discharge at the centre of a closed spherical vessel of bronze, of 4 litres capacity, having its interior highly polished. Records of the pressures developed and their rates of development were obtained, and the results are summarised in the following tables, the term " molecular ratio " denoting the ratio of the number of molecules in unit volume at the moment of maximum temperature to the initial number.

Table I.

Mixtures of Ethylene and Air.

Theoretical mixture for complete combustion: 6·53% C_2H_4.
Approximate limits of inflammability: 3·4—16% C_2H_4.

Ethylene, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
4·14	0·042	0·092	5·58
4·45	0·035	0·070	6·29
4·86	0·027	0·051	6·74
5·07	0·022	0·044	6·67
5·10	0·020	0·040	6·80
6·18	0·012	0·029	7·71
6·60	0·009	0·0265	7·70
6·82	0·010	0·027	7·91
7·57	0·010	0·028	7·96
7·94	0·013	0·029	7·96
8·04	0·014	0·030	8·12
8·20	0·013	0·027	8·12
9·50	0·020	0·050	7·76
10·36	0·026	0·068	7·45

Calculated Maximum Temperatures and Pressures.

C_2H_4, %.	Products of combustion at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
6	8·64	2·97	12·81	0·43	3·30	71·85	1·0173	2437°	8·56
7	7·72	5·65	14·13	0·82	1·74	69·94	1·0333	2530	9·07
7·5	7·22	6·92	14·64	1·13	1·05	69·04	1·0420	2555	9·24
8	6·42	8·50	14·98	1·58	0·62	67·90	1·0531	2560	9·37
9	4·60	11·79	14·97	2·99	0·12	65·53	1·0798	2505	9·40
10	3·19	14·52	13·94	5·31	0·02	63·02	1·1101	2415	9·29

Table II.

Mixtures of Propylene and Air.

Theoretical mixture for complete combustion: 4·44% C_3H_6.
Approximate limits of inflammability: 2—8% C_3H_6.

Propylene, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
3·18	0·059	0·098	5·69
3·22	0·057	0·096	5·92
3·40	0·049	0·080	6·32
3·42	0·032	0·078	6·70
3·50	0·033	0·068	6·79
3·82	0·023	0·060	7·20
4·28	0·027	0·049	7·12
4·64	0·023	0·044	7·48
4·89	0·023	0·040	7·54
5·45	0·024	0·043	7·65
5·67	0·026	0·046	7·66
6·06	0·035	0·059	7·47
6·58	0·063	0·101	7·35
6·89	0·056	0·113	7·05
7·54	0·102	0·256	5·68
7·65	0·115	0·380	5·18
7·84	0·153	0·470	4·40

TABLE II (*contd.*).

Calculated Maximum Temperatures and Pressures.

C_3H_6, %.	Products of combustion at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
3·5	9·11	0·97	11·63	0·13	4·78	73·28	1·0228	2235°	7·90
4·5	9·00	3·69	13·83	0·48	1·84	71·16	1·0439	2445	8·85
4·8	8·37	5·06	14·28	0·76	1·33	70·20	1·0543	2460	9·00
5·1	7·82	6·30	14·76	1·00	0·76	69·36	1·0640	2467	9·13
5·8	6·09	9·56	14·99	2·22	0·13	67·01	1·0929	2425	9·24
6·5	4·23	12·78	14·34	4·17	0·01	64·47	1·1274	2315	9·12
7·0	3·28	14·63	13·46	5·94	Trace	62·69	1·1529	2217	8·98

TABLE III.

Mixtures of Butylene and Air.

Theoretical mixture for complete combustion: 3·37% C_4H_8.
Approximate limits of inflammability: 2—6% C_4H_8.

C_4H_8, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·14	0·091	0·193	5·30
2·39	0·063	0·107	5·84
2·58	0·040	0·088	6·40
3·07	0·027	0·056	7·34
3·65	0·021	0·045	7·95
4·07	0·019	0·041	8·03
4·23	0·020	0·042	7·94
4·44	0·023	0·046	7·82
4·53	0·023	0·048	7·95
4·65	0·026	0·056	7·96
5·21	0·040	0·087	7·65
5·27	0·048	0·094	7·38
5·84	0·073	0·181	6·75
6·53	0·128	0·564	4·54

Calculated Maximum Temperatures and Pressures.

C_4H_8, %.	Products of combustion at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
3·0	9·36	1·99	12·73	0·26	3·26	72·40	1·0412	2337°	8·45
3·5	8·80	4·20	14·00	0·60	1·65	70·75	1·0598	2430	8·94
3·85	8·05	6·05	14·75	0·94	0·73	69·48	1·0755	2455	9·19
4·2	6·87	8·22	15·05	1·59	0·25	68·02	1·0950	2435	9·29
5·0	4·08	13·01	14·27	4·30	0·01	64·33	1·1486	2272	9·15

The Pressures developed.—In Fig. 1 a graphical comparison is made of the variation of maximum pressure, both calculated and observed, with composition of the mixtures. In Table IV are given data, obtained from Fig. 1, comparing the observed and the calculated maximum pressures and recording the amounts of "lost pressure" expressed as percentages of the calculated values. The theoretical mixtures for complete combustion are recorded in the first column of the table. As with the paraffins, there is with each

olefin a marked "displacement" of the observed maximum-pressure mixture, from the theoretical mixture for complete combustion, towards excess of hydrocarbon. These displacements can only be attributed to the effects of dissociation, since the calculated values, for which an allowance is made for dissociation, are similarly displaced.

FIG. 1.

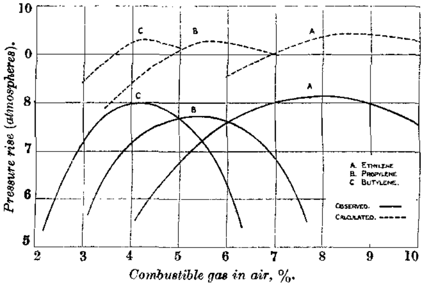


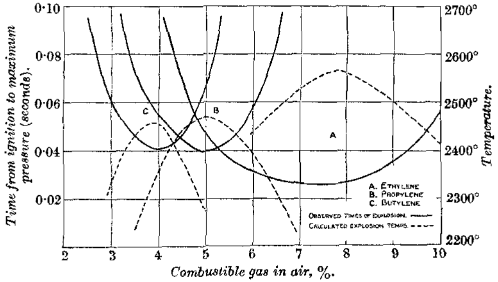
TABLE IV.

	Theoretical mixture for complete combustion, %.	Mixture giving maximum press., %. Calc.	Mixture giving maximum press., %. Obs.	Maximum press., atm. Calc.	Maximum press., atm. Obs.	Lost press., %.
C_2H_4 ...	6·53	8·35	8·25	9·42	8·15	13·6
C_3H_6 ...	4·44	5·50	5·45	9·28	7·75	16·5
C_4H_8 ...	3·37	4·20	4·20	9·30	8·00	14·0

The "lost pressures" are greater than were calculated for the paraffins, for which the highest value, with methane, was 9·8%. Whilst this result may be due to errors in the data used in the calculations, it is possible that the loss of heat during explosion of the olefins is higher than with the paraffins, either through greater radiation or by reason of less complete combustion at the moment of maximum pressure. As regards possible errors in the data, we have previously pointed out that Bjerrum's values for the mean specific heats of steam are probably too low over the temperature range concerned (*loc. cit.*; and J., 1928, 15). There is no reason to believe, however, that the error thus introduced into the calculations would be more marked at the somewhat higher temperatures attained on explosion of olefin–air mixtures, for Bjerrum's values increase rapidly with temperature over this range (2000—3000°).

On the other hand, it does not seem probable that conduction losses can materially affect the pressures attained under the conditions of experiment, except with mixtures near the limits of inflammability (in which flame does not spread spherically from the point of ignition) or with such mixtures as exhibit considerable "after-burning." None of the time–pressure records with the olefin–air mixtures showed the flattened crest, or initial retardation of the cooling curve, usually associated with "after-burning." On the whole, higher radiation losses, due to the higher explosion-temperatures attained, would seem to be the most reasonable explanation of the greater "lost pressures."

Fig. 2.



The Rate of Development of Pressure.—Fig. 2 shows the effect of composition of the mixtures on the "time of explosion" (the interval between ignition and the attainment of maximum pressure) and on the (calculated) explosion-temperatures. Table V, compiled from Fig. 2, makes comparison between the observed "maximum-speed" mixtures and the calculated "maximum-temperature" mixtures. The "maximum-speed" mixture for each gas is that for which the "time of explosion" is least.

Table V.

Composition of Maximum-speed and Maximum-temperature Mixtures.

	Olefin in max.-speed mixture (obs.), %.	Olefin in max.-temp. mixture (calc.), %.	Mean temp., calc.	Time (obs.) from ignition to maximum pressure (sec.).
C_2H_4	7·6	7·8	2563°	0·026
C_3H_6	5·0	5·0	2468	0·040
C_4H_8	4·0	3·9	2457	0·041

As with the paraffins (*loc. cit.*), the close correspondence between the observed values for the maximum-speed mixtures and the calculated values for the maximum-temperature mixtures shows that, for mixtures of a given combustible gas with air, flame temperature is the controlling factor in determining the mean rate of development of pressure. From recent experiments by Miss E. M. Georgeson and Mr. F. J. Hartwell (private communication), it is evident that the speed of the uniform movement of flame in mixtures of the olefins with air is also controlled mainly by the flame temperature, for the compositions of the maximum-speed mixtures (see Table VI) are the same as in our experiments. The order of speed of the flames is also the same.

TABLE VI.

Uniform Movement in Olefin–Air Mixtures.

(Georgeson and Hartwell.)

	Olefin in maximum-speed mixture (obs.), %.	Speed (cm./sec.) of uniform movement (obs.) (2·5-cm. diam. tube).
Ethylene ...	7·6	165
Propylene ...	5·1	101
Butylene ...	4·0	98

The displacement of the maximum-temperature mixture from that for complete combustion towards excess of inflammable gas, deduced by Tizard and Pye (Empire Motor Fuels Committee, Report, 1923—24) and by ourselves, has recently been observed experimentally by Loomis and Perrott (*Ind. Eng. Chem.*, 1928, **20**, 1004), who find that the methane–air and propane–air mixtures giving the highest flame temperatures contain 9·8% of methane and 4·2% of propane. Our calculated values (*loc. cit.*, p. 2078) were 10·0% and 4·4% respectively; whilst the mixtures for complete combustion contain 9·47% and 4·0%, respectively.

EXPERIMENTAL.

The apparatus and mode of procedure were as for the experiments on the inflammation of mixtures of the paraffins and air (see also J., 1918, **113**, 844). The gases were obtained commercially and purified by liquefaction and fractional distillation until the theoretical values for the ratio C/A were obtained on explosion analysis (C = contraction; A = subsequent absorption by potassium hydroxide solution). The butylene consisted of normal and *iso*-hydrocarbons in nearly equal proportion.

Calculations.—The method of calculation of maximum temperatures and pressures, and the data used were as for the paraffins, with the following additional data for heats of combustion (lower

values) at constant volume: Ethylene 325·3, propylene 462·3, butylene 610·2 kg.-cals. per g.-mol.

Note.—In our paper on the pressures produced on inflammation of mixtures of carbon monoxide and air (J., 1928, 17), the following correction should be made with respect to the dissociation of carbon dioxide: "Expressed as percentages, the corresponding values at 1 atm. and 2543° K are: Fenning and Tizard, 13·8; Bjerrum, 20·7; Maxwell and Wheeler, 25·6." The correction in no way affects the argument advanced in the paper.

DEPARTMENT OF FUEL TECHNOLOGY,
SHEFFIELD UNIVERSITY. [*Received, December 21st*, 1928.]

XXXVIII.—*2-Substituted Derivatives of* p-*Cresol.*

By MAURICE COPISAROW.

HOLLEMAN and HOEFLAKE (*Rec. trav. chim.*, 1916, **36**, 270) have shown that *p*-cresol is convertible into its 2-nitro-derivative [Me in position 1] by nitration of its carbonate and subsequent hydrolysis, but their procedure, as well as that described in D.R.-P. 206638 (Friedländer, "Fortschritte in der Teerfarbenfabrikation," IX, 151), is not entirely satisfactory, and the modifications now described enable much better yields to be obtained.

The methyl ether of 2-nitro-*p*-cresol was obtained in good yield by the action of methyl sulphate on (*a*) 2-nitro-*p*-cresol and (*b*) 2-nitro-*p*-tolyl carbonate in alkaline medium under atmospheric pressure. This compares well with Knecht's method (*Annalen*, 1882, **215**, 88; *Ber.*, 1882, **15**, 1072) of heating potassium 2-nitro-*p*-tolyloxide with methyl iodide *under pressure*. The methyl ether of 2-amino-*p*-cresol (*iso*cresidine) was obtained in 78—82% yield by reducing the methyl ether of 2-nitro-*p*-cresol with iron filings in an acid medium, instead of tin and hydrochloric acid (Knecht, *loc. cit.*).

2-Amino-*p*-cresol was obtained by the direct and simultaneous reduction and hydrolysis of 2-nitro-*p*-tolyl carbonate with (*a*) sodium sulphide and (*b*) less satisfactorily with iron filings in acid medium, a process entirely different from and simpler than those of Knecht (*Annalen*, 1882, **215**, 91; *Ber.*, 1882, **15**, 300), Wallach (*Ber.*, 1882, **15**, 2834), and Maasen (*Ber.*, 1884, **17**, 610), who obtained the substance by diazotisation of 2 : 4-tolylenediamine.

EXPERIMENTAL.

***p*-Tolyl carbonate**, m. p. 113° after crystallising from alcohol, was obtained in 98% yield by passing carbonyl chloride into a stirred solution of *p*-cresol (108 g.) and sodium hydroxide (42 g.)

in water (500 c.c.) maintained at 40—50°; when the gas was no longer absorbed, the product was triturated with cold aqueous sodium hydroxide (3—5%), washed, and dried below 100°. Below 30°, *p*-tolyl chloroformate also was produced in the reaction, and above 60° hydrolysis of the *p*-tolyl carbonate took place.

A mixture of sulphuric acid (240 g. of 99—100% H_2SO_4) and nitric acid (2·12 mols. of 86—92% acid) at 10—12° was gradually added to a stirred solution of *p*-tolyl carbonate (240 g.) in 99—100% sulphuric acid (1200 g.) at 12—15°. The mixture, after being stirred for 2 hours at 18—20°, was poured on ice (2 kg.). The crude pressed material was boiled with aqueous sodium carbonate (200 g. in 2 l. of water) for 2 hours, the solution at once acidified at 35°, and the 3-nitro-*p*-cresol removed by distillation in steam. The residual 2-nitro-isomeride (yield, 79%), after being decolorised in benzene or alcohol with animal charcoal, was obtained in yellow odourless crystals, m. p. 76—77°.

A mixture of 2-nitro-*p*-cresol (153 g.), toluene (300 c.c.), methyl sulphate (140 g.), and anhydrous sodium carbonate (127 g.) was heated and stirred at 110—112° for 4—5 hours. On steam distillation the toluene came over, followed by 2-nitro-*p*-tolyl methyl ether as a pale yellow oil (yield, 77%).

A mixture of the crude 2-nitro-*p*-cresol from 120 g. of *p*-tolyl carbonate with toluene was dried by distilling off all but 300 c.c. of the latter. The residual solution was treated at 50—60° with methyl sulphate (140 g.) and sodium carbonate (160 g.), and the whole stirred and heated at 110—112° for 4—5 hours. The yield of methyl ether was 60% of the *p*-tolyl carbonate used. The ethyl ether was prepared in a similar manner.

2-Amino-*p*-cresol was obtained from a similar quantity of the above crude nitration product, after removal of traces of 3-nitro-*p*-cresol in steam, by the gradual addition of a solution of crystallised sodium sulphide (480 g.) in water (1600 c.c.) to a thin paste of the material in water (100 c.c.) at 40°. The reduction was completed in 4—5 hours at 90—95°, and the mixture was then acidified, boiled to remove hydrogen sulphide and sulphur dioxide, and neutralised. The total yield corresponded to 79% of the carbonate used, but one-fifth of this remained in solution. Recrystallised from ether, the product was obtained in colourless crystals, m. p. 157—159°.

*iso*Cresidine (2-amino-*p*-tolyl methyl ether) resulted from the reduction at 95—98°, in a reflux apparatus, of 2-nitro-*p*-tolyl methyl ether (167 g.) in water (600 c.c.) and glacial acetic acid (15—20 c.c.) by the gradual addition of iron filings (170 g.) during 2—3 hours. Isolation of the product by steam distillation gave a

pure product but involved loss owing to the solubility of the base even in brine. Extraction of the reduction mixture with toluene and precipitation of the base in the form of its hydrochloride gave a better yield but a less pure product.

p-Tolyl chloroformate (compare Barrel and Morel, *Compt. rend.*, 1899, **128**, 1578; Pickard and Littlebury, J., 1907, **91**, 302) is best prepared by passing carbonyl chloride into a stirred solution of *p*-cresol (108 g.) and sodium hydroxide (42—44 g.) in water (500 c.c.), maintained below 10°. The oily product boils at 108°/30 mm. (yield, 78—80%).

The author wishes to express his indebtedness to Mr. George E. McKenlay, B.Sc. (Tech.), for assistance in connexion with this work.

THE UNIVERSITY, MANCHESTER. [*Received, October 13th*, 1928.]

XXXIX.—*The Chlorination of Phthalic Acid in Alkaline Solution.*

By ERNEST EDWARD AYLING.

THE chlorination of phthalic acid in alkaline solution, first described by Auerbach (*Chem.-Ztg.*, 1880, **4**, 407) and confirmed by Zincke and Schmidt (*Ber.*, 1894, **27**, 741), was shown by Egerer and Meyer (*Monatsh.*, 1913, **34**, 81) to yield 4-chlorophthalic acid. Moore, Marrack, and Proud (J., 1921, **119**, 1788), in preparing the latter by this method, could not obtain it sufficiently pure for analysis. From the divergence in the analyses and constants given by the above workers for the chloro-acid and its anhydride, and also from their disagreement with the values obtained for these compounds, when prepared by other methods (compare Beilstein, "Handbuch der Organische Chemie," IV Aufl., IX, 816; Bogert and Renshaw, *J. Amer. Chem. Soc.*, 1908, **30**, 113; von Braun, *Ber.*, 1923, **56**, 2332), it would appear that the pure acid cannot be readily obtained by the direct chlorination method. It seemed of interest, therefore, to submit the method to a closer investigation.

The chlorination proceeds most satisfactorily with 3 molecules excess of potassium hydroxide. The precipitated potassium hydrogen salts consist mainly of 4-chlorophthalate together with a little phthalate and some 4 : 5-dichlorophthalate, which has not been previously recognised in this reaction and was identified through the anhydride. The earlier workers (Auerbach; Egerer and Meyer;

Zincke and Schmidt, *locc. cit.*) give no clue as to the excess of alkali employed, and Moore, Marrack, and Proud (*loc. cit.*) recommend the use of 5 molecules excess of sodium hydroxide. This quantity, however, was found to yield a product containing a much larger proportion of dichlorophthalate, which could not be removed entirely by the methods of purification recommended, and its presence would account for the observation of Moore, Marrack, and Proud that chloride is retained, and for the high chlorine content of the 4-chloro-anhydride found by Egerer and Meyer.

The separation of 4-chlorophthalic acid from admixed phthalic and 4 : 5-dichlorophthalic acids by means of solvents, as recommended by previous workers, was not found practicable owing to the small difference in solubility of the chloro-acids. Conversion of the mixed acids into their methyl esters, however, gave a mixture which was readily separated by distillation under reduced pressure, the methyl 4-chlorophthalate obtained yielding pure 4-chlorophthalic acid, m. p. 151°.

The formation of the chlorophthalic acid by this method has been ascribed (Egerer and Meyer, *loc. cit.*) to the action of the hypochlorite first formed. This type of action, however, is generally associated with amines, acid amides and imides, and hydroxy-compounds only. Hypochlorite solution has no action on a neutral phthalate solution, whereas chlorine yields chlorophthalates, the yield of precipitated salts being, however, small, the greater portion of the chlorophthalates remainiug in solution. The chlorination, therefore, is not dependent on the presence of the excess of alkali but results from the direct action of chlorine upou the phthalate in solution. The larger yields of precipitated acid salts obtained when excess of alkali is used show that the latter serves for the ready isolation of the chlorinated products, which are salted out by the alkali chloride formed. This view is supported by the different results obtained with sodium hydroxide and potassium hydroxide. Comparative experiments show that the chlorinated product contains much more dichlorophthalate when the former is used, and this difference, which has not been previously observed, can only result from solubility differences. Potassium hydrogen 4-chlorophthalate can only be sparingly soluble under the experimental conditions and is precipitated before much dichlorination can take place, whereas the sodium hydrogen 4-chlorophthalate must be more soluble, remaining in solution while further chlorination occurs.

EXPERIMENTAL.

Chlorination of the Alkaline Phthalate Solution.—A rapid stream of chlorine was passed into an ice-cooled solution of 16·6 g. of

phthalic acid in 200 c.c. of water containing 28 g. of potassium hydroxide (3 mols. excess) until no apparent further precipitation of acid potassium salt occurred; on standing, a small additional quantity separated (total yield, 19 g. or 80%). The acid salt was dissolved in 40% sulphuric acid, and the solution extracted with ether, the extract yielding the crude acid, m. p. 141—150° (Found: equiv. by titration with baryta, 99·6. Calc., 100·25). Examination of the crude acid (*a*) by fractional precipitation from aqueous solution by means of hydrochloric acid (compare Crossley and Renouf, J., 1906, **89**, 1552), (*b*) by fractional extraction with benzene (compare Auerbach; Egerer and Meyer, *locc. cit.*), and (*c*) by conversion into the anhydride by means of acetyl chloride and fractional crystallisation of the anhydride from carbon tetrachloride, failed to yield a monochloro-compound free from dichloro-. Under (*a*) and (*b*) phthalic acid was the least soluble, and under (*c*) the least soluble fractions ultimately yielded 4 : 5-dichlorophthalic anhydride, m. p. 187° (compare Villiger, *Ber.*, 1909, **42**, 3532) (Found: Cl, 32·8. Calc.: Cl, 32·7%). This m. p. was unchanged by admixture with 4 : 5-dichlorophthalic anhydride prepared from 4 : 5-dichloro-*o*-xylene (Hinkel, Ayling, and Bevan, J., 1928, 1876).

Separation by the Esterification Method.—The crude chloro-acid, m. p. 141—150°, was esterified in the usual manner with methyl alcohol and hydrogen chloride, the excess of alcohol removed under reduced pressure, and the residue poured into water. Extraction with ether yielded a thick liquid which only solidified to a white mass on cooling in a freezing mixture. Distillation under reduced pressure yielded methyl 4-chlorophthalate, b. p. 186—187°/32 mm., which solidified when cooled with ice and crystallised from well-cooled light petroleum (b. p. 40—60°) in fine white needles, m. p. 38° (Rée, *Annalen*, 1886, **233**, 236; Graebe and Rée, J., 1886, **49**, 527, give 37°) (Found: Cl, 15·6. Calc.: Cl, 15·5%).

Hydrolysis of the methyl 4-chlorophthalate by the usual method yielded 4-chlorophthalic acid, m. p. 151°, unchanged by recrystallisation from carbon tetrachloride or benzene (von Braun, *loc. cit.*, gives 157° for the acid obtained from ethyl 4-chlorophthalate) (Found: Cl, 17·5. Calc.: Cl, 17·7%). No retention of solvent was observed and it is possible that the observation of Moore, Marrack, and Proud (*loc. cit.*) was due to the acetic acid used in conjunction with the benzene.

4-Chlorophthalic anhydride, obtained from the acid by means of acetyl chloride, crystallised from carbon tetrachloride in small plates, m. p. 97° (Found: Cl, 19·7. Calc.: Cl, 19·5%).

Comparative Experiments with Sodium and Potassium Hydroxides. —Chlorine was passed simultaneously through two solutions each of 16·6 g. of phthalic acid in 200 c.c. of water, containing 24 g. of sodium hydroxide (4 mols. excess) in the one case and 33·6 g. of potassium hydroxide (4 mols. excess) in the other. The chlorination and the isolation of the crude acid were carried out as described above.

	NaOH expt.	KOH expt.
Yield of acid salt	19·9 g.	16·3 g.
Calc. for monochlorophthalate	22·25 g.	23·85 g.
Mol. wt. of acid salt (by baryta)	243·1	240·2
Calc. for monochlorophthalate	222·5	238·5
M. p. of crude acid	153—156°	145—148°
Equivalent of acid (by baryta)	107·3	100·0

Monochlorophthalic acid requires : m. p. 151°; equiv. 100·25.

The author desires to express his thanks to Dr. L. E. Hinkel for his advice and for helpful criticism during the progress of this work.

UNIVERSITY COLLEGE, SWANSEA. [*Received, December 8th,* 1928.]

XL.—*The Structure of Organic Molecular Compounds.*

By GEORGE MACDONALD BENNETT and GERVASE HEWITSON WILLIS.

THE formulation of organic additive compounds by means of the electronic theory of valency follows at once in many cases from Sidgwick's interpretation (J., 1923, **123**, 725) of Werner's theory. A number of other complexes, particularly those formed by the union of two different organic substances, cannot be simply represented in this manner and have been generally regarded as having their constituent molecules united by means of molecular rather than atomic forces. The union is, in fact, attributed to the action of the fields of residual valency of either molecules or groups of atoms (Pfeiffer, "Organische Molekülverbindungen," 2nd ed., 1927, p. 23; Kremann, *Ahrens Vorträge*, 1924, **27**, 58, 78). Forces such as these may indeed account for the cohesion of a liquid and for the stable association of molecnles in a crystal, but where molecular compounds exist in the liquid phase their components must be held together more firmly than by residual valency. We shall assume that the union is by means of covalent linkages, a point of view which has also been adopted by Lowry (*Chem. and Ind.*, 1924, **43**, 218).

A variety of evidence is available to show that many organic

molecular compounds persist in solution. Behrend (*Z. physikal. Chem.*, 1894, **15**, 183) and Brown (J., 1925, **127**, 345) have shown that the compounds of picric acid and trinitrotoluene with hydrocarbons are only partly dissociated in solution. The relationships between the composition of mixtures and their physical properties such as freezing point (Kremann and Grasser, *Monatsh.*, 1916, **37**, 761) or viscosity (Bramley, J., 1916, **109**, 10, 434, 469) point to the occurrence of complexes in the liquid. The compounds $CHCl_3,Et_2O$ and $Me_2CO,PhOH$, the presence of which in the mixed liquids was deduced from the vapour-pressure curve (Dolezalek and Schulze, *Z. physikal. Chem.*, 1913, **83**, 45; Weissenberger, Schuster, and others, *Monatsh.*, 1925, **46**, 47, 295), have been proved to exist by means of freezing-point curves (Smits and Berckmans, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 401; Schmidlin and Lang, *Ber.*, 1910, **43**, 2806).

Considerable importance also attaches to the occurrence of visible colour. This has been a valuable indication of the presence of compounds in solution (Werner, *Ber.*, 1909, **42**, 4324; Pfeiffer, *Annalen*, 1924, **440**, 265). Moreover, when two organic substances together yield a solid having a colour much deeper than that of the components, this (apart from any consideration of the liquid phase) *is evidence of the formation of a true molecular compound.* If the union of these molecules depended merely on the more complete saturation of their stray fields of residual valency, a decrease rather than an increase of colour should result.

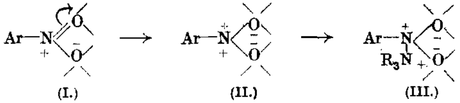
The molecular ratio in which organic substances combine is in most cases a simple one (1 : 1 or 2 : 1, usually the former). The occurrence of any simple stoicheiometric ratio is strong evidence against the residual valency theory of union. Yet the formation of the equimolecular compound between, for example, trinitrobenzene and quinoline (Sudborough and Beard, J., 1910, **97**, 773) has been regarded as evidence in favour of this indefinite type of attachment on the ground that direct union of a molecule of quinoline with one nitro-group must lead to a similar reaction with all three such groups and the formation of a complex with the molecular ratio 1 : 3. But this is not necessarily to be expected according to the electronic theory. The formation of a dative bond to one of the nitro-groups will introduce a new electrical dipole at the point of attachment. Further combination at a second adjacent group (to yield a 1 : 2 compound) would now be opposed by a certain extra force, since the creation of the new bond must involve the introduction of another similar dipole near the first. Thus the second and third nitro-groups may remain unattached (although they will contribute by their general polar effects to the stability of the

complex formed through the first nitro-group). The case may be compared with that of the monomethiodides of diazines and 1 : 4-dithian (see Bennett and Hock, J., 1927, 2496). These considerations are of general application and account for a tendency towards simplicity of molecular ratios in complexes. Less simple ratios are, nevertheless, observed in some cases, and these are theoretically possible up to the limit set by the numbers of active groups present in the molecules which unite.

An important group of organic molecular compounds results from the union of nitro-compounds on the one hand with various amines, aromatic hydrocarbons or their derivatives on the other. The most stable and numerous of these are formed from bases : moreover the union of the nitro-compound with the base is clearly analogous to the combination of acid and base. Kremann has, in fact, called amines and hydrocarbons heteropolar with respect to nitro-compounds. This implies that the amine is the donor molecule, the nitro-compound the acceptor, and the union would appear to be through the basic nitrogen atom and the nitro-group.

That the nitro-group itself is involved follows, as Werner showed (*loc. cit.*), from the formation of similar compounds by tetranitromethane. Pfeiffer contends (*Annalen*, 1916, **412**, 253) that the amine is attached through the aromatic nucleus, but his arguments are not convincing. The direct participation of the basic group in the union is, moreover, indicated by the coloration developed by polynitro-compounds with alcoholic ammonia (compare, for example, Kenner and Parkin, J., 1920, **117**, 852) and by the coloured compound of piperidine with trinitroanisole (Giua, Marcellino, and Curti, *Gazzetta*, 1920, **50**, 300), for no point of attachment but the basic group is conceivable in the case of ammonia or a saturated amine. Certain physical properties of the nitrobenzyldialkylamines, to be described presently, also support our view of the union through both the nitro-group and the amino-nitrogen.

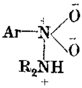
The union may be represented as occurring after a preliminary activation of the nitro-compound (I), the resulting form (II) uniting



(I.) (II.) (III.)

with a tertiary amine by accepting from it its lone pair of electrons to give the complex (III), in which each nitrogen atom carries a single positive charge and each oxygen atom a negative one. Thus

the structure is to some extent stabilised by the fact that each charge has near to it an opposite charge on an adjacent atom. The corresponding complex (IV) produced from a secondary or primary amine may pass into the second form (V) by the movement of one proton.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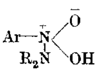
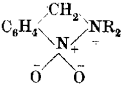

(V.)


(VI.)

Formula (V) is identical with that recently suggested by Brewin and Turner for coloured intermediates in reactions between secondary amines and nitro-compounds (J., 1928, 336).

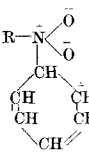
From this point of view it appeared to follow that the *o*-nitrobenzyldialkylamines would show intramolecular co-ordination as in (VI), and any corresponding self-co-ordination in the *m*- and *p*-isomerides would necessarily be *inter*-molecular. The *o*-isomeride should therefore have a somewhat lower boiling point than the others and differences in solubility might also arise (compare Sidgwick and Callow, J., 1924, **125**, 527). The three isomeric nitrobenzyldiethylamines do in fact show a marked difference of volatility, boiling at 175—177° (*o*-), 206—208° (*m*-) and 219—221° (*p*-) under 42 mm. pressure (Noelting and Kregczy, *Bull. Soc. chim.*, 1916, **19**, 336). We have redetermined and confirmed this difference and have also found a similar difference for the three isomeric nitrobenzyldimethylamines. The solubility curves of naphthalene in the three nitrobenzyldiethylamines and of these three (liquid) nitroamines in trimethylene glycol over a limited range are shown in Figs. 1 and 2. In each case the *m*- and *p*-isomerides have almost identical solubilities and the *o*-isomeride differs to a small but definite extent.

The similarity in type of the complexes formed by polynitro-compounds with bases and with hydrocarbons justifies the assumption that the function of the latter is analogous to that of bases. The hydrocarbon, like the base, is a donor molecule. This property appears to be characteristic of the ethylene group, as may be seen from the platinum complexes

$$[PtCl_2,NH_3,C_2H_4] \text{ and } [PtCl_3,C_2H_4]K,H_2O$$

(Jörgensen, *Z. anorg. Chem.*, 1900, **24**, 153), in which the molecule of ethylene functions as the equivalent of a molecule of ammonia in the co-ordination sphere. A single ethylene bond can thus provide one covalency, but the considerations advanced above provide an adequate explanation of the fact that the three actual or potential

double bonds in the benzene nucleus also, in general, provide only one covalency. This is the case in the complex $[Ni(CN)_2,NH_3,C_6H_6]$ and others of the same type (Hofmann and Küspert, *Z. anorg. Chem.*, 1897, **15**, 203) and it also seems to be the rule with the compounds of trinitrobenzene. With substances containing several separate aromatic nuclei (not fused together), each tends to attach one molecule of trinitrobenzene to itself (Sudborough, J., 1916, **109**, 1341).



(VII.)

The union of benzene with a nitro-compound may be represented as in (VII), one ethylene bond having reacted in the polarised form —$\overset{|\,-}{\text{CH}}$—$\overset{+}{\text{CH}}$—. The negative charges on the oxygen atoms may help to stabilise the positive charge on the nuclear carbon atom, the structure being of the betaine type. This positively charged tervalent carbon atom is partly responsible for the deep colour developed, the case being similar to that of the triarylmethyl ion and the metal ketyls.

The well-known fact that nitro-compounds containing several nitro-groups, such as trinitrobenzene and trinitrotoluene, yield the most stable additive compounds with hydrocarbons and bases is to be attributed to the influence of other such groups in assisting the one active group to function. Any group which attracts electrons (any " electron sink ") should be able to contribute to the stability of such complexes, so that carbomethoxy- or sulphonyl chloride groups might be substituted for one or two of the nitro-groups of the complex. Complexes of this kind derived from mononitro-compounds have been hitherto unknown, but we find that, in agreement with the considerations advanced above, methyl 5-nitro*iso*phthalate forms an orange crystalline *compound* with α-naphthylamine. Several mononitro- and dinitro-sulphonyl chlorides have, moreover, been described in the literature as crystallising with (usually one molecular proportion of) benzene, toluene, or xylene and must be regarded as instances of the complex formation now under discussion—namely, nitrobenzene-3 : 5-disulphonyl chloride (Heinzelmann, *Annalen*, 1877, **188**, 164), 4-nitronaphthalene-2 : 6- and -2 : 7-disulphonyl chlorides (Beilstein, " Organische Chemie," 4th edn, vol. XI, pp. 216, 218), 4 : 5-dinitronaphthalene-2 : 7-disulphonyl chloride (*op. cit.*, p. 218), and 4 : 5-dinitronaphthalene-2-sulphonyl chloride (*op. cit.*, p. 189). We have subjected the first of these to a closer investigation and have obtained pale yellow *compounds* of it with toluene and mesitylene and bright yellow *compounds*

with naphthalene and anisole. It also combines with bases of the quinoline series.

The molecular compounds of picric acid with bases or hydrocarbons fall into two classes. The picrates of relatively strong bases have a characteristic bright yellow colour and are formulated by Pfeiffer as $(NO_2)_3C_6H_2{\cdot}OH \ldots NC_nH_m$ (*op. cit.*, p. 343). As this colour is also shown by quaternary ammonium and trialkylsulphonium picrates, it must be attributed to the picrate ion, and the complexes should be written $[BH]^+ [C_6H_2(NO_2)_3{\cdot}O]^-$. Complexes of the second class are formed by picric acid with weak bases or hydrocarbons and usually have a deeper colour. In these the union is presumably through one nitro-group of the picric acid in the way already discussed, but in the case of bases an electrovalent union is conceivable with the picrate ion in an isomeric form,

$$O{:}C_6H_2(NO_2)_2{:}NO_2^-.$$

Some such alternative modes of attachment must be involved in the "complex isomerism" of the yellow and red forms of *o*-bromoaniline picrate (Hertel, *Annalen*, 1927, **451**, 179) and in the contrast between the bright yellow picrate of 2 : 4-dichloroaniline and the deep red *compound* of *s*-trichloroaniline and picric acid which we have isolated. This is evidently a closely connected, if not an identical phenomenon with that of the existence of the red and yellow thallium picrates and salts of the nitrophenols.

The large group of complexes formed by the union of benzoquinone or its substituted derivatives with aromatic hydrocarbons, amines, and phenols has developed from the study of the smaller group known as the quinhydrones. The function of the amines and hydrocarbons being necessarily to donate, it follows that the quinone is the acceptor-component in these molecular compounds. This is in agreement with the fact (Pfeiffer, *op. cit.*, pp. 290 *et seq.*) that introduction of halogen into the nucleus of the quinone enhances its power of forming such compounds and the depth of colour of the products. The polar effect of the halogen would facilitate the acceptance of electrons but would oppose their donation (the chloroanilines are weaker bases than aniline). That quinone does not readily act as a donor is, moreover, shown by the fact that it does not combine with picric acid. In compounds of quinones with bases, neither the halogen atoms nor hydrogen attached to nitrogen is essential to the existence of a complex, for we have isolated coloured compounds of benzoquinone itself with the tertiary amines *pp'*-tetramethyldiaminodiphenylmethane and *pp'*-tetramethyldiaminodiphenylcarbinol. The molecular ratio in these complexes (2 of base : 1 of quinone) indicates that only one of the two dimethylamino-groups in the molecule of the base is functioning, the

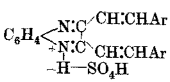
case being analogous to that of the polynitro-compounds discussed above.

This property of quinones was attributed by Kurt Meyer (*Ber.*, 1909, **42**, 1149; 1910, **43**, 157) to the carbonyl group and particularly to the oxygen atom of that group. The same view is adopted by Pfeiffer. It is, however, impossible to suppose that this oxygen atom should accept electrons : the carbonyl group can in fact only do so if it becomes activated to the form $>\overset{+}{C}-\overset{-}{O}$ in which free positive affinity is developed on the carbon atom. Union with a tertiary base should therefore yield the complex $>C\begin{matrix}\overset{-}{O}\\ |\\ NR_3\end{matrix}$, and a complex with an aromatic hydrocarbon may be similarly represented by a formula analogous to that (VII) of the nitro-compound complex. *A consideration of the formulæ for quinhydrones to* which this conception points is reserved for a future communication.

The halochromic properties of the quinones displayed in presence of concentrated sulphuric acid are influenced by substituents in exactly the opposite sense. The intensity and depth of colour produced are decreased by those substituents which increase the stability and the depth of colour of the quinone complexes referred to above (Pfeiffer, *op. cit.*, p. 286), and conversely with groups of opposite general polar character. This contrast is to be expected, for the halochromic effects are to be attributed to the molecular compounds of the quinone and sulphuric acid formed by donation from the ketonic oxygen atom to the hydrogen of the acid which becomes doubly co-ordinated : $>C{=}\underset{+}{O}-\underset{-}{H}-SO_4H$. The function of the quinone is thus the reverse of that which it performs when uniting with an aromatic molecule and the polar influences are consequently also in opposite directions.

The variations in depth of colour of the complexes and also of the halochromic effects, not only in the instance just referred to but also among substituted aromatic ketones and quinoline bases (*Pfeiffer, op. cit., pp. 66—85, 191), are throughout in the directions* to he expected from the nature of the substituent groups if Pfeiffer's conception of the origin of the colour is accepted. The colour is in fact connected with the positive unsaturation developed on the carbon atom doubly bound in these substances to oxygen or nitrogen, as a result of the co-ordination of the oxygen or nitrogen atom with the acid present. As an illustration we may refer to the halochromic effects, which we now record, of a series of styrylquinoxalines

recently prepared (J., 1928, 1960). The coloured complex involved is of the annexed type. The unsubstituted substance (Ar = Ph) gives a deep reddish-purple colour in sulphuric acid which disappears on dilution. The colour with the nitrostyryl bases (Ar = $C_6H_4 \cdot NO_2$) is less deep, that with methoxystyryl derivatives (Ar = $C_6H_4 \cdot OMe$) deeper than with the parent substance. This bathochromic effect of the methoxy-group and the opposed hypsochromic effect of the nitro-group are the result of their respective polar effects, which favour or hinder, respectively, the essential co-ordination of the nitrogen atom with the acid. Moreover, the observations recorded show clearly that these two groups each have an increased effect when in the *o*- or *p*-position in the phenyl group as compared with that exercised in the *m*-position. This "alternating effect" is as usual satisfactorily explained by the superposition of the inductive and tautomeric electronic effects in the *o*- and *p*-positions but not in the *m*-position.



Finally, reference must he made to the class of organic complexes in which the separate molecules are united through a halogen atom. These are usually addition compounds of ether or an amine with various halogen compounds, particularly chloroform and iodoform. Examples of this type are the relatively stable ether–chloroform complex $CHCl_3,Et_2O$ (Smits and Berckmans, *loc. cit.*; compare also Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 48), the quinoline–iodoform compound $CHI_3,3C_9H_7N$, which has long been known (Rhoussopoulos, *Ber.*, 1883, **16**, 202), and chloroform or chloral addition compounds of bases such as toluquinaldine, herberine, quinine, phenylacridine, and colchicine. These compounds must be held together hy a dative bond from the nitrogen (or oxygen) atom to a halogen atom. The latter becomes 2-covalent as happens in a variety of other cases, the tendency to do this increasing from chlorine to iodine (Sidgwick, "The Electronic Theory of Valency," pp. 291—293). The numerous addition compounds of organic ammonium, sulphonium, arsonium, and stibonium iodides with one molecular proportion of iodoform (Steinkopf and others, *Ber.*, 1921, **54**, 2969; *J. pr. Chem.*, 1925, **109**, 230) may be included in this class of complex and regarded as analogous to potassium tri-iodide, KI_3, having the structure $[R_nM]^+(I-\overset{\vee}{\underset{|}{I}}-CHI_2)^-$. The simple complexes of amines with halogen compounds are of considerable theoretical importance, as there can be little doubt that the first step in the union of an amine or sulphide with an alkyl halide is the formation of compounds of this kind, which are sub-

sequently transformed into the ammonium or sulphonium halide. This mechanism of reaction accounts for the fact that alkyl iodides react in such cases faster than the chlorides.

EXPERIMENTAL.

Preparation and Examination of the Nitrobenzyldiethyl- and dimethyl-amines.—The *o*-, *m*-, and *p*-nitrobenzyldiethylamines were prepared by the action of an excess of diethylamine on the respective nitrobenzyl chlorides (yield, 70—85%). The products were yellow oils (the *o*-isomeride having a more intense colour than the others), which were redistilled twice under comparable conditions in the same apparatus. The *o*-nitrobenzyldiethylamine had b. p. 144°/13 mm. (picrate, m. p. 117°). The *p*-isomeride had b. p. 160°/13 mm. (picrate, m. p. 131°). The *m*-isomeride had b. p. 158°/13 mm. and gave a picrate of m. p. 151° (Found : N, 16·2. Calc. : N, 16·0%). Noelting and Kregczy give this m. p. as 161°.

The three nitrobenzyldimethylamines were prepared from the respective nitrobenzyl chlorides in each case by two methods : (*a*) as described by Goss, Ingold, and Wilson (J., 1926, 2458), hexamethylenetetramine being used (yield, 50—60%), and (*b*) by means of dimethylamine hydrochloride and alkali in alcoholic solution as for the diethyl bases (yield, 60%). The substances obtained by the two methods were identical. They were yellow oils (the *o*-isomeride having a more intense colour than the others), and were redistilled twice under comparable conditions in the same apparatus. o-*Nitrobenzyldimethylamine* (Found : N, 16·1. $C_9H_{12}O_2N_2$ requires N, 15·6%) yielded a *hydrochloride*, colourless crystals, m. p. 215°, readily soluble in water (Found : Cl, 16·4. $C_9H_{12}O_2N_2$,HCl requires Cl, 16·4%), and a *picrate*, readily soluble in boiling ethyl alcohol, from which it crystallised in small yellow plates, m. p. 143° (Found : N, 17·4. $C_{15}H_{15}O_9N_5$ requires N, 17·1%). The *m*-isomeride yielded a *picrate*, bright yellow, microscopic crystals, m. p. 217°, sparingly soluble in boiling ethyl alcohol (Found : N, 17·5%). The *p*-isomeride gave a *picrate* crystallising in bright yellow prisms, m. p. 149°, sparingly soluble in hot ethyl alcohol (Found : N, 17·4%).

These six substances were also examined by the method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1412) in order to obtain a more accurate comparison of their vapour pressures or boiling points. Unfortunately, however, the compounds showed signs of slow decomposition at the temperatures used, so these observations are less precise than was desired. They serve, however, to confirm the definite difference in boiling point. The figures are in the following table :

Nitrobenzyldimethylamines :

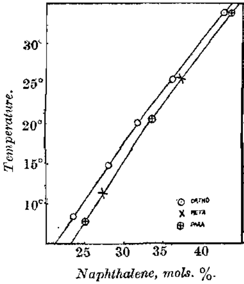
	B. p. observed in distillation.	B. p. by Smith and Menzies' method.
o	133°/16 mm.	116—117°/11 mm.
m	144°/16 mm.	130—132°/10 mm.
p	146°/16 mm.	131—133°/10 mm.

Nitrobenzyldiethylamines :

o	144°/13 mm.	124—127°/10 mm.
m	158°/13 mm.	139—142°/10 mm.
p	160°/13 mm.	146—148°/10 mm.

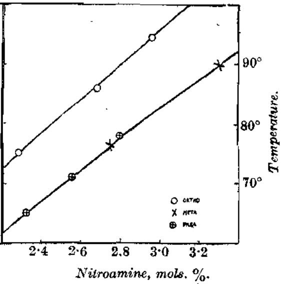
Measurements of Solubility with the Nitrobenzyldiethylamines.—The method used for the determination of the solubility of naphth-

FIG. 1.



Solubilities of naphthalene in isomeric nitrobenzyldiethylamines.

FIG. 2.



Solubilities of isomeric (liquid) nitrobenzyldiethylamines in trimethylene glycol.

alene was that of Ward (*J. Physical Chem.*, 1926, **30**, 1316). The naphthalene was carefully purified, and melted at 80·05—80·07°. The thermometer was graduated in 0·1° and had been recently standardised. The results are given in Table I and plotted in Fig. 1.

The determinations of solubility of the amines in trimethylene glycol were of necessity less precise. The critical solution temperatures of the mixtures could not be determined with greater accuracy than 0·5—1°. The range of observations was limited by the small solubility of the amine in the glycol and by the fact that signs of decomposition appeared when the mixtures were heated for long above 100°. The glycol was repeatedly fractionated, and distilled constantly at 214° (uncorr.). The observations are given in Table II and plotted in Fig. 2.

TABLE I.

Solubilities of Naphthalene in Isomeric Nitrobenzyldiethylamines.

p-Isomeride :						
Naphthalene, mols. % ...	24·97	33·58	43·56	52·29		
Temperature	7·7°	20·5°	33·9°	43·5°		
m-Isomeride :						
Naphthalene, mols. % ...	27·32	37·19	46·85			
Temperature	11·3°	25·7°	37·5°			
o-Isomeride :						
Naphthalene, mols. % ...	23·54	27·97	31·86	36·23	42·76	50·13
Temperature	8·4°	14·9°	20·1°	25·5°	33·9°	42·3°

TABLE II.

Solubilities of Isomeric Nitrobenzyldiethylamines in Trimethylene Glycol.

p-Isomeride :	Nitroamine, mols. %	2·32	2·55	2·80
	Temperature	65°	71°	78°
m-Isomeride :	Nitroamine, mols. %	2·75	3·30	
	Temperature	76·5°	90°	
o-Isomeride :	Nitroamine, mols. %	2·28	2·68	2·96
	Temperature	75°	86°	94·5°

Addition Compound of Methyl 5-*Nitro*iso*phthalate*.—The colourless ester is dissolved in a warm solution of α-naphthylamine in light petroleum, saturated in the cold; the molecular *compound*, $C_6H_3(NO_2)(CO_2Me)_2,C_{10}H_7{\cdot}NH_2$, separates, on cooling, in orange crystals, m. p. 82° (Found : N, 7·6. $C_{20}H_{18}O_6N_2$ requires N, 7·3%).

Addition Compounds of 5-*Nitrobenzene*-1 : 3-*disulphonyl Chloride.* —The required nitrodisulphonic acid was obtained by heating benzene with oleum (60% SO_3; 2 mols.) at 210—230° for 4 hours, cooling, adding an excess (50—100 c.c.) of fuming nitric acid, and boiling under reflux for 8 hours. The crystalline acid deposited from the cold solution (yield, 50%) was converted, by warming with an excess of phosphorus pentachloride, into the disulphonyl chloride.

The nitrobenzenedisulphonyl chloride is obtained in almost colourless crystals, m. p. 97—98°, from carbon tetrachloride (Fonnd : Cl, 21·85. Calc. : Cl, 22·2%). The large yellow crystals from toluene are a compound with one molecule of the latter (Found : Cl, 17·7. Calc. : Cl, 17·3%). These crystals effloresce rapidly on keeping. From mesitylene, lemon-yellow prisms, m. p. 68—70°, of a *compound* with one molecular proportion of the hydrocarbon are obtained (Found : Cl, 16·4. $C_{15}H_{15}O_6NCl_2S_2$ requires Cl, 16·1%). They effloresce on keeping. From anisole there are deposited bright yellow prisms of the *compound* (mol. ratio 1 : 1) which melts indefinitely at 55—60° (Found : Cl, 16·3. $C_{13}H_{11}O_7NCl_2S_2$ requires Cl, 16·6%). The crystals become opaque on keeping. The *compound* with naphthalene (mol. ratio 1 : 1) is obtained in tufts of

bright yellow needles, m. p. 102—103°, by crystallising the components together from carbon tetrachloride (Found: Cl, 15·7. $C_{16}H_{11}O_6NCl_2S_2$ requires Cl, 15·8%).

The acid chloride dissolves with considerable evolution of heat in pure dry quinoline to form dark-coloured viscous solutions. A similar behaviour is shown with other tertiary bases, but no analytically pure compound has yet been separated.

Addition Compounds of Benzoquinone with Two Bases.—Absolute ethyl alcohol, saturated with benzoquinone and *pp'*-tetramethyldiaminodiphenylcarbinol at laboratory temperature and filtered, deposited, on keeping, a *compound*, $C_6H_4O_2,2C_{17}H_{22}ON_2$, in large, intensely dark green prisms, m. p. 169—170° (Found: N, 8·7. $C_{40}H_{48}O_4N_4$ requires N, 8·6%).

Xylene, saturated with benzoquinone and *pp'*-tetramethyldiaminodiphenylmethane, yielded in similar manner, after 1 week, a *compound*, $C_6H_4O_2,2C_{17}H_{22}N_2$, in pale purple prisms, m. p. 71° (Found: N, 9·0. $C_{40}H_{48}O_2N_4$ requires N, 9·1%).

Picrate of s-*Trichloroaniline.*—This substance was obtained from its components in ethyl alcohol or benzene–light petroleum solution and crystallised in long, deep red needles, m. p. 80—83° (Found: picric acid, 53·4. Mol. ratio 1 : 1 requires picric acid, 53·8%).

Preparation of 3-*Styryl*-2-*methylquinoxaline.*—Althougb attempts to isolate this substance bad previously been unsuccessful (Bennett and Willis, J., 1928, 1968), we subsequently obtained it in good yield as follows: 2 : 3-Dimethylquinoxaline is heated, with seven times its weight of a mixture of equal volumes of benzaldehyde and benzyl alcohol or nitrobenzene, at 180° for ½ hour. The chief product is 3-*styryl*-2-*methylquinoxaline*, which is isolated by removing other substances in a current of steam. It crystallises in clusters of pale yellow bipyramids, m. p. 137° (Found: N, 11·7. $C_{17}H_{14}N_2$ requires N, 11·3%). It dissolves in concentrated sulphuric acid with an intense reddish-purple colour, which fades to an orange-yellow on dilution with water.

Comparative Colorations of Styrylquinoxalines with Sulphuric Acid.—The method used by Stobbe and Haertel (*Annalen*, 1909, **370**, 99) in observing the halochromic effects of ketones was adopted, except that a greater dilution of the substance was necessary owing to the greater intensity of the colours developed with these styrylquinoxalines. Actually, 0·5 c.c. of concentrated sulphuric acid was added to a solution of 0·00002 mol. of the quinoxaline derivative in methyl acetate (5 c.c.). The colour produced is recorded in column 3 of Table III, and the figures in column 4 are the comparative volumes of water required to discharge this colour to a permanent pale yellow or orange tint.

TABLE III.

Base.	Colour in H_2SO_4.	Colour with H_2SO_4 in methyl acetate.	"Basicity."
Styrylmethyl-quinoxaline	Reddish-purple	—	—
Distyryl-	Reddish-purple	Orange-red	1·0
Di(*p*-nitrostyryl)-	Orange-red	Brownish-orange	—
Di(*m*-nitrostyryl)-	Scarlet	Orange	—
Di(o-nitrostyryl)-	Orange-red	Lemon-yellow	—
m-Nitrostyrylmethyl-	Orange-red	Yellow	—
2 : 4-Dinitrostyrylmethyl-	Yellow-orange	—	—
2 : 4 : 6-Trinitrostyrylmethyl- ...	Yellow	—	—
Di(*o*-iodostyryl)-	Reddish-purple	Orange	0·5
Di(*o*-chlorostyryl)-	Reddish-purple	Reddish-orange	0·9
Di(*m*-chlorostyryl)-	Reddish-purple	Orange	0·5
Di(*p*-chlorostyryl)-	Reddish-violet	Orange-red	1·1
o-Methoxystyrylmethyl-	Magenta	Rose-red	2·5
m-Methoxystyrylmethyl-	Orange-red	Orange-red	1·4
p-Methoxystyrylmethyl-	Violet	Intense violet	4·3
Di(*p*-methoxystyryl)-	Prussian-blue	—	—
Di(3 : 4-dimethoxystyryl)-	Pale blue	—	—
Methylenedioxystyrylmethyl- ...	Prussian-blue	Purple-blue	4·7
Di(methylenedioxystyryl)-	Blue-green	Purple-blue	4·9
Di(*β*-furylvinyl)-	Mulberry	Mulberry	3·6
2 : 3-Distyryl-6-methyl-	Reddish-purple	—	—
Di(*m*-nitrostyryl)-6-methyl-	Scarlet	—	—
Di(2 : 4-dinitrostyryl)-6-methyl-	Orange	—	—
2-(*p*-Methoxystyryl)-3 : 6-dimethyl-	Violet	—	—
Di(methylenedioxystyryl)-6-methyl-	Prussian-blue	—	—
o-Nitrostyryl-	Orange-red	—	—
m-Nitrostyryl-	Scarlet	—	—
p-Nitrostyryl-	Orange-red	—	—
2 : 4-Dinitrostyryl-	Orange-yellow	—	—

We are indebted to Miss V. M. Thorn and Mr. F. S. Statham for carrying out some of the analyses recorded in this paper, and to the Chemical Society for assistance in the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, November 30th*, 1928.]

XLI.—*Some Derivatives of the Aliphatic Glycols.*

By GEORGE MACDONALD BENNETT and FREDERICK HEATHCOAT.

THE halohydrins of the glycols and their acyl derivatives and ethers of the types $AcO\cdot[CH_2]_n\cdot X$, $RO\cdot[CH_2]_n\cdot X$, and $ArO\cdot[CH_2]_n\cdot X$ (where X is a halogen atom) are important synthetic reagents. In the course of the preparation of γ-, δ-, and ϵ-substituted chloro-sulphides we have made use of several new compounds of this class, the preparation and properties of which we now describe.

The chlorohydrins of ethylene and trimethylene glycols are most conveniently prepared by the action of sulphur monochloride on the glycol as originally recommended for the former by Carius

(*Annalen*, 1862, **124**, 257). We have extended this reaction to tetra- and penta-methylene glycols and have obtained their chlorohydrins, but only in poor yields and in an impure state, as they decompose when redistilled under diminished pressure with liberation of hydrogen chloride and presumably of the corresponding polymethylene oxide. The *α-naphthylurethanes* of *δ-chlorobutyl* and *ε-chloroamyl alcohols* were, however, isolated.

The only substances of the type $AcO{\cdot}[CH_2]_n{\cdot}X$, where $n = 4$ or 5, hitherto known were the δ-bromobutyl and ε-bromoamyl benzoates (von Braun, *Ber.*, 1913, **46**, 1782). The conversion of trimethylene glycol into γ-chloropropyl acetate by means of acetyl chloride at 100° was recently described by Bogert and Slocum (*J. Amer. Chem. Soc.*, 1924, **46**, 763). By applying this reaction to the two higher glycols we have obtained *δ-chlorobutyl* and *ε-chloroamyl acetates* in quantity. These substances have proved suitable for the syntheses we had in view and by their means we have isolated *phenyl* and *ethyl δ-hydroxybutyl sulphides* and *phenyl* and *methyl ε-hydroxyamyl sulphides*. The chloro-sulphides derived from these hydroxy-sulphides are under investigation and will be described in a subsequent communication.

For certain purposes the ethers of the halohydrins are of particular value: for example, phenyl β-bromoethyl ether (Bentley, Haworth, and Perkin, J., 1896, **69**, 169; Mills and Bains, J., 1925, **127**, 2503), benzyl chloroethyl ether, and methyl iodoethyl ether (Bennett, J., 1925, **127**, 1277). A convenient method of preparation of methyl β-chloroethyl ether, which we now record, is therefore of interest. On the other hand, we have been unable to confirm the experiments of Foran (*J. Soc. Chem. Ind.*, 1925, **44**, 173) on the preparation of bromodiethyl ether.

Several ethers of this general type, derived from the higher glycols, are known, the most accessible and useful being phenyl δ-bromobutyl ether (von Braun, *loc. cit.*) and benzyl γ-chloropropyl and δ-chlorobutyl ethers (J., 1927, 472).

We have taken the opportunity of completing the series of bisphenylurethanes and bis-α-naphthylurethanes of the glycols up to pentamethylene glycol and of the α-naphthylurethanes of the corresponding chlorohydrins (compare Bickel and French, *J. Amer. Chem. Soc.*, 1926, **48**, 747). The melting points are tabulated below:

Glycol.	Ethylene.	Tri-methylene.	Tetra-methylene.	Penta-methylene.
Bisnaphthylurethane	176°	164°	198°	147°
Bisphenylurethane ...	157·5	137·5	180	174
Naphthylurethane of chlorohydrin	101	76	66	72

It may be noted that an alternation of higher and lower melting points occurs in the bisurethanes in which the lengthening chain is terminated by large polar groups, whereas the melting points fall with little or no alternation if the large highly polar group is at one end only. This appears to be a general phenomenon: *e.g.*, the dibenzoates of the glycols show an alternation of melting point, whereas the *p*-nitrobenzoates or the *p*-nitrobenzyl phthalates (Reid, *J. Amer. Chem. Soc.*, 1917, **39**, 1249) of the simple alcohols show a continuous fall of melting point.

EXPERIMENTAL.

Methyl β-Chloroethyl Ether.—Glycol monomethyl ether (57 g.), dissolved in dimethylaniline (109 g.), was cooled while thionyl chloride (98 g.) was added slowly through an upright condenser. The mixture was left over-night, dilute hydrochloric acid added, and the product extracted with ether. The ethereal solution was dried and distilled. The chloro-ether (28 g.) boiled at 90·5°/747 mm. and had $d_{4^\circ}^{0^\circ}$ 1·056 and $d_{4^\circ}^{20^\circ}$ 1·031. The substance dissolves in water to the extent of 8% by weight at laboratory temperature.

Attempt to repeat Foran's Preparation of Bromodiethyl Ether.—The account given (Foran, *loc. cit.*) of the action of sodium ethoxide on ethylene dibromide was unconvincing, because it was hardly to be expected that the product of b. p. 128° would be separated sufficiently by distillation from ethylene dibromide (b. p. 131°) and diethoxyethane (b. p. 123·5°), both of which must be present. No evidence of any kind as to the homogeneity of the product was recorded, nor was any analysis reported. We therefore tried to repeat this experiment, but could not isolate any appreciable amount of the fraction in question. In the original, 18 g. of sodium are described as being dissolved in 45 c.c. of absolute alcohol. As this was found to be impossible, the latter figure is probably a misprint. We used either 180 c.c. or 450 c.c. of alcohol. The chief product of the reaction appears to be vinyl bromide, which escapes. Finally we abandoned the attempt to obtain enough of the liquid to test its homogeneity.

Ethylene and Trimethylene Chlorohydrins.—The liquid obtained by Carius's method (*loc. cit.*) is filtered from the sulphur and subjected at once to fractional distillation. The addition of pieces of marble on redistillation is advantageous. This reaction with trimethylene glycol was first mentioned by Derick and Bissell (*J. Amer. Chem. Soc.*, 1916, **38**, 2478) and is recommended by Gough and King (J., 1928, 2439). It renders trimethylene chlorobromide a readily accessible substance (compare Conant, Segur, and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 1882).

By the action of 3 : 5-dinitrobenzoyl chloride on trimethylene chlorohydrin we obtained *γ-chloropropyl* 3 : 5-*dinitrobenzoate*, which formed colourless plates, m. p. 77°, from light petroleum (Found : N, 10·0; Cl, 12·1. $C_{10}H_9O_6N_2Cl$ requires N, 9·7; Cl, 12·3%).

γ-Chloropropyl Acetate.—Trimethylene glycol (37 g.) and acetic anhydride (1 mol.) were heated for a few minutes on the steam-bath, the acetic acid was distilled off under diminished pressure, and sulphur chloride (1 mol.) added. After the mixture had been heated at 100° for 4 hours, it was fractionated; the liquid of b. p. 66°/14 mm. was pure δ-chloropropyl acetate (yield, 68%) (Found : Cl, 26·3. Calc. : Cl, 26·5%).

γ-Hydroxydipropyl Sulphide.—Propyl mercaptan (1 mol.), γ-chloropropyl acetate (1 mol.), and sodium hydroxide (1 mol. in aqueous alcohol) were heated under reflux for 1 hour. An excess of alkali was then added and the mixture boiled to hydrolyse the ester. The solvent was distilled in steam, the product removed in ether, and the aqueous liquor further extracted twice with this solvent. The extracts were dried over sodium sulphate and distilled. *γ-Hydroxydipropyl sulphide* was obtained as an oil of characteristic, unpleasant odour, b. p. 112°/16 mm. (yield, 54%) (Found : S, 23·6. $C_6H_{14}OS$ requires S, 23·9%). The liquid, which is sparingly soluble in water, had $d_{4°}^{20°}$ (vac.) 0·9794, $n_{\alpha}^{20°}$ 1·47789, whence $[R_L]_\alpha$ = 38·91 (calc., 39·21). It was converted by phenylcarbimide into the *phenylurethane*, $C_3H_7{\cdot}S{\cdot}C_3H_6{\cdot}O{\cdot}CO{\cdot}NHPh$, which formed colourless microscopic plates, m. p. 36° (Found : N, 5·8. $C_{13}H_{19}O_2NS$ requires N, 5·5%). β-Hydroxyethyl butyl sulphide (Whitner and Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 636) yields the isomeric *phenylurethane*, $C_4H_9{\cdot}S{\cdot}C_2H_4{\cdot}O{\cdot}CO{\cdot}NHPh$, which forms colourless plates, m. p. 44·5°, from light petroleum (Found : N, 5·9%).

Tetramethylene Glycol.—The glycol was prepared from the mixture of the dibromide with benzonitrile obtained by von Braun and Lemke's method (*Ber.*, 1922, **55**, 3526). This mixture (a quantity found by density measurements to contain 100 g. of the dibromide) was heated under reflux for 4—5 hours with potassium acetate (100 g.) and glacial acetic acid (33 g.) and then distilled under diminished pressure. Benzonitrile was removed from the product by fractional distillation at atmospheric pressure with a good column, the portion boiling above 210° being practically pure tetramethylene diacetate. This ester (100 g.) was heated at 160—170° for 3 hours with calcium hydroxide (36 g. of calcium oxide with 25 g. of water), the pressure reduced, and the product distilled off. The liquid was subjected to the same process with half the amount of lime and after a final redistillation the pure glycol was obtained, b.p. 127°/20 mm., which solidified on standing (yield, 61%).

The *bis-α-naphthylurethane* of this glycol was crystallised twice from *n*-butyl alcohol, from which it separated in colourless needles with a straight extinction, m. p. 198° (Found : N, 6·4. $C_{26}H_{24}O_4N_2$ requires N, 6·5%).

The Action of Sulphur Monochloride on Tetramethylene Glycol.—The glycol (30 g.) and sulphur chloride (38 g.; 0·85 mol.) were warmed together on the steam-bath for 6 hours and then at 150° in an oil-bath for 3 hours. The sulphur having been removed by filtration, the liquid and the acetone washings of the sulphur were distilled. A fraction boiling at 86°/15 mm. (yield, 15 g.) consisted of crude *δ-chlorobutyl alcohol*, but when this was redistilled (under reduced pressure) it disappeared, much hydrogen chloride being produced. From the crude liquid the *α-naphthylurethane* of *δ-chlorobutyl alcohol* was isolated by heating it with α-naphthylcarbimide for 1 hour at 100°. It crystallised from light petroleum in minute colourless plates, m. p. 66° (Found : Cl, 12·9. $C_{15}H_{16}O_2NCl$ requires Cl, 12·8%).

δ-Chlorobutyl Acetate.—A stout-walled tube, containing tetramethylene glycol (10—15 g.) and an inner tube containing acetyl chloride (1 mol.), was sealed and heated in a boiling water-bath for 8 hours. The cold product was rinsed out with acetone and, after two distillations, pure *δ-chlorobutyl acetate* was obtained as a colourless liquid of pleasant odour, b. p. 87°/17 mm., 98°/32 mm. (yield, 88%) (Found : Cl, 23·5. $C_6H_{11}O_2Cl$ requires Cl, 23·55%).

This substance is also obtainable by heating the glycol with sulphur chloride and acetylating the product. The following physical constants were observed: $d_{4°}^{0°}$ (vac.) 1·1024, $d_{4°}^{20°}$ (vac.) 1·0803; $n_{\alpha}^{20°}$ 1·43811, $n_{\beta}^{20°}$ 1·44369, $n_{\gamma}^{20°}$ 1·45130; whence $[R_L]_{\alpha}$ = 36·6 (calc., 36·2), $[R_L]_{\beta}$ = 37·00 (calc., 36·78), and $[R_L]_{\gamma}$ = 37·55 (calc., 37·10).

Condensation of Ethyl and Phenyl Mercaptans with δ-Chlorobutyl Acetate.—Chlorobutyl acetate (15 g. in 20 c.c. of methyl alcohol) was added to a solution of ethyl mercaptan (6·5 g.) and potassium hydroxide (6 g. in 6 c.c. of water and 10 c.c. of methyl alcohol), and the mixture boiled under reflux for ½ hour. Potassium hydroxide (10 g. in aqueous alcohol) was added, and boiling continued for ½ hour to hydrolyse the ester. The liquid was then acidified with acetic acid, and the alcohol evaporated. The upper layer of oil was removed, and the aqueous phase twice extracted with ether. The solution was dried over sodium sulphate and distilled in a vacuum. *Ethyl δ-hydroxybutyl sulphide* was obtained as a colourless oil of characteristic, unpleasant odour, b. p. 120°/19 mm. (yield, 71%) (Found : S, 23·7. $C_6H_{14}OS$ requires S, 23·9%). The liquid

had $d_4^{20^\circ}$ (vac.) 0·9794, $n_\alpha^{20^\circ}$ 1·48118, whence $[R_L]_\alpha = 39·00$ (calc., 39·21).

The *phenylurethane*, $EtS·[CH_2]_4·O·CO·NHPh$, forms colourless microscopic plates, m. p. 37° (Found : N, 5·9. $C_{13}H_{19}O_2NS$ requires N, 5·5%).

Chlorobutyl acetate (10 g.) was added to a solution of thiophenol (7·3 g.) in alcoholic potassium hydroxide (3·8 g. in aqueous methyl alcohol) and the mixture was boiled for ½ hour and then for a further equal period after the addition of more alkali (7·6 g. of potassium hydroxide). The whole was finally acidified with acetic acid, and the alcohol distilled off. A little water was added to dissolve salts which had separated, the upper layer was removed, and the solution twice extracted with ether. The ethereal solution was washed with water, dried over sodium sulphate, and evaporated. The residue, after being heated at 100° in a stream of air at 20 mm., solidified. This *phenyl δ-hydroxybutyl sulphide* crystallised from *light petroleum in colourless needles*, m. p. 24° (yield, 96%) (Found : S, 17·4. $C_{10}H_{14}OS$ requires S, 17·6%). It was insoluble in water, but readily soluble in most organic solvents. Phenylcarbimide readily converted it into the *phenylurethane*, $PhS·[CH_2]_4·O·CO·NHPh$, which formed colourless plates, m. p. 68·5°, from light petroleum (Found : N, 4·9. $C_{17}H_{19}O_2NS$ requires N, 4·65%).

Pentamethylene Glycol.—The mixture of pentamethylene dibromide and benzonitrile obtained by the action of phosphorus pentabromide on benzoylpiperidine (yield, 50%) was converted through the diacetate into the glycol by the method given for its lower homologue above (yield, 90%).

The glycol readily reacted with phenyl- and α-naphthyl-carbimides. The *bisphenylurethane*, $NHPh·CO·O·[CH_2]_5·O·CO·NHPh$, crystallised *thrice from ethyl alcohol, formed minute colourless needles*, m. p. 174° (Found : N, 8·5. $C_{19}H_{22}O_4N_2$ requires N, 8·2%). The *bis-α-naphthylurethane* was obtained in colourless microscopic plates, m. p. 147° (Found : N, 6·5. $C_{27}H_{26}O_4N_2$ requires N, 6·3%).

The Action of Sulphur Chloride on Pentamethylene Glycol.—The glycol (30 g.) was heated, as in the case of the lower homologue, with sulphur chloride (35 g. ; 0·9 mol.). A fraction of b. p. 114°/16 mm. was separated and redistilled (12·5 g.) (Found : Cl, 36·1. $C_5H_{11}OCl$ requires Cl, 28·9%). This liquid was free from hydrogen chloride but evidently contained pentamethylene dichloride. From it was isolated the *α-naphthylurethane* of *ε-chloroamyl alcohol*, $C_{10}H_7·NH·CO·O·[CH_2]_5Cl$, in colourless needles, m. p. 72° (Found : Cl, 12·2. $C_{16}H_{18}O_2NCl$ requires Cl, 12·15%).

ε-Chloroamyl Acetate.—The reaction between pentamethylene

glycol and acetyl chloride was carried out as with the lower homologue. The product differed in that it contained a large amount of free hydrogen chloride. After two distillations the fraction of b. p. 104°/20 mm. was separated and redistilled, finally with a little acetic anhydride to acetylate any chlorohydrin present. ε-*Chloroamyl acetate* was isolated as a colourless liquid of pleasant odour, b. p. 103°/18 mm. (yield, 41%) (Found: Cl, 21·8. $C_7H_{13}O_2Cl$ requires Cl, 21·6%). The substance has $d_{4^\circ}^{20^\circ}$ (vac.) 1·0648, $n_{\alpha}^{20^\circ}$ 1·43791, whence $[R_L]_{\alpha}$ = 40·56 (calc., 40·79).

Condensation of Methyl and Phenyl Mercaptans with ε-*Chloroamyl Acetate.*—Methyl mercaptan, prepared as described by Arndt (*Ber.*, 1921, **54**, 2236), was passed into methyl alcohol cooled in a good freezing mixture. To this solution, potassium hydroxide (4·2 g. in 5 c.c. of water and 20 c.c. of methyl alcohol) and chloroamyl acetate (12·3 g.) were added and the mixture was boiled for ½ hour. An excess of alkali was added, and the boiling repeated to hydrolyse the ester. The product was isolated as described for the isomeric ethyl hydroxybutyl sulphide. *Methyl* ε-*hydroxyamyl sulphide* was obtained as a colourless oil of unpleasant odour, b. p. 121°/16 mm. (Found: S, 23·75. $C_6H_{14}OS$ requires S, 23·9%) (yield, 56%). The liquid has $d_{4^\circ}^{20^\circ}$ (vac.) 0·9846, $n_{\alpha}^{20^\circ}$ 1·488185, whence $[R_L]_{\alpha}$ = 39·44 (calc., 39·21), and is converted by phenylcarbimide at 100° into the *phenylurethane*, $MeS\cdot[CH_2]_5\cdot O\cdot CO\cdot NHPh$, which forms colourless microscopic plates, m. p. 43·5° (Found: N, 5·9. $C_{13}H_{19}O_2NS$ requires N, 5·5%).

The condensation with thiophenol was carried out as with the lower homologue. *Phenyl* ε-*hydroxyamyl sulphide*, $PhS\cdot[CH_2]_5\cdot OH$, was obtained in flat colourless needles, m. p. 31·5°, from light petroleum (Found: S, 16·3. $C_{11}H_{16}OS$ requires S, 16·3%). It is almost insoluble in water, soluble in most organic solvents. The *phenylurethane*, $PhS\cdot[CH_2]_5\cdot O\cdot CO\cdot NHPh$, crystallises from light petroleum in colourless plates, m. p. 59° (Found: N, 4·7. $C_{18}H_{21}O_2NS$ requires N, 4·45%).

We are indebted to the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in this work, and to the Chemical Society for assistance in the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, December 6th, 1928.*]

XLII.—*The Vapour Density and Pressure of Ammonium Iodide.*

By Ronald H. Purcell and Wilhelmus de Lange.

The first determinations of the vapour density of ammonium iodide vapour were carried out by Deville and Troost (*Compt. rend.*, 1859, **49**, 255; 1863, **56**, 891), who found that the unsaturated vapour was 96% dissociated at 440° and 80% at 860°. No further values were available until Smith and Lombard (*J. Amer. Chem. Soc.*, 1915, **37**, 2055) determined the density of the saturated vapour between 300° and 380°. Their figures indicate that there is only slight dissociation above 340°, and that there is actually association below this temperature. Similar work for ammonium chloride and bromide has been shown to be inaccurate (Braune and Knoke, *Z. physikal. Chem.*, 1928, **135**, 49; Smits and Purcell, J., 1928, 2936; Smits and de Lange, *ibid.*, p. 2944), and since trustworthy values were required in connexion with the work on intensive drying it was thought necessary to redetermine the vapour densities.

The vapour pressure of ammonium iodide has been determined by Johnson (*Z. physikal. Chem.*, 1908, **65**, 36) and by Smith and Calvert (*J. Amer. Chem. Soc.*, 1914, **36**, 1363). The differences in the values they recorded were considerable, amounting to more than 12 cm. at the higher temperatures. Smith and Calvert attributed this to the use of a sealed apparatus by Johnson, which, they maintained, would cause the further dissociation, $2HI = H_2 + I_2$, to affect his measurements. Johnson had, however, shown that the rate of formation of iodine was small compared with his rate of working. The results described subsequently agree very well with those of Smith and Calvert, but were obtained in a sealed apparatus. Consequently, *it is more probable that the difference was due to* some impurity in the sample of salt used by Johnson.

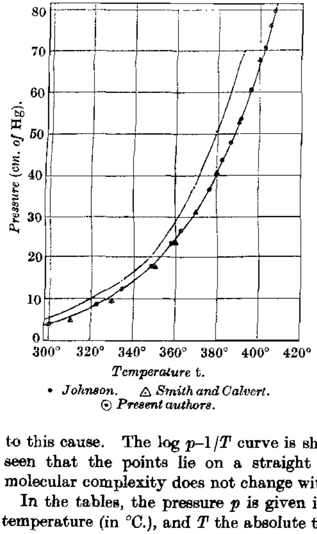
The experimental method used in this research was identical with the second one used by Smits and his co-workers (*locc. cit.*) for ammonium bromide and chloride. The ammonium iodide used was a sample of the purest salt supplied by E. de Häen. It was further purified by sublimation in high vacuum. If the salt was heated to 200° in an electric furnace and was thoroughly dry, there was hardly any decomposition, as was shown by the fact that only a trace of iodine collected in the liquid-air trap. The product was powdered and stored over solid potash.

Preliminary experiments, carried out with an excess of salt, showed that the rate of decomposition of hydrogen iodide was negligible if the apparatus had been carefully cleaned and the water

removed from the glass walls, prior to filling, by heating to dull redness in a stream of dry oxygen. Consequently, this precaution was always taken. The salt was weighed in through a side tube in a counter-stream of dry gas, and the tube melted off, the apparatus re-evacuated, and finally sealed off from the pumps (for details, see Smits and Purcell, *loc. cit.*).

The vapour pressure was first determined in an apparatus of approximately 30 c.c. capacity containing an excess of ammonium iodide. The results of these measurements are given in Table I and plotted in Fig. 1, and they are seen to be in good agreement with those of Smith and Calvert. The pressures, at the lower temperatures, obtained at the end of the experiment agree with those taken at the beginning, thus showing that there was no appreciable formation of iodine. Also the experiment was carried out in a fused-salt bath in a 4-litre Pyrex beaker so that any iodine vapour could have been readily seen; actually, none was observed. Hence the slight difference between our values and those of Smith and Calvert at lower temperatures caunot be ascribed to this cause. The log p–$1/T$ curve is shown in Fig. 2. It will be seen that the points lie on a straight line, indicating that the molecular complexity does not change with temperature.

Fig. 1.



In the tables, the pressure p is given in cm. of mercury, t is the temperature (in °C.), and T the absolute temperature.

Table I.

p.	t.	p.	t.	p.	t.	p.	t.
4·0	299·1°	36·4	376·8°	70·5	402·5°	20·4	352·3°
5·8	310·3	43·6	382·6	60·4	395·8	12·3	334·5
13·8	339·2	48·6	386·4	47·9	386·4	8·5	322·4
17·8	348·5	53·6	399·1	42·8	381·6	6·1	311·2
23·4	357·9	60·7	395·8	26·3	362·6		

A series of determinations of the vapour density of the saturated vapour between 340° and 400° was then carried out. The results of these experiments are given in Tables II—VI. The volume, V, of the apparatus and the weight, W, of the ammonium iodide introduced are also recorded. The volume was obtained by weighing the apparatus dry and also when full of water, and is correct to 0·1 c.c.

TABLE II.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
8·3	323·1°	0·919	1678	13·9	351·4°	1·143	1602
9·6	325·7	0·982	1670	13·8	347·8	1·140	1611
10·8	332·1	1·033	1653	13·7	342·0	1·137	1626
13·9	347·8	1·143	1611	13·4	337·6	1·127	1638
14·2	356·2	1·152	1589	10·4	328·9	1·017	1661

(V = 314·7 c.c.; W = 0·0809 g.)

TABLE III.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
11·8	334·6°	1·075	1646	26·1	375·9°	1·417	1541
17·4	348·3	1·241	1610	25·6	366·4	1·408	1564
24·2	359·3	1·384	1581	25·6	364·9	1·408	1568
26·6	385·4	1·425	1519	25·5	363·1	1·407	1572
27·1	394·0	1·433	1499	21·7	355·9	1·336	1590
27·3	402·9	1·436	1480	14·7	342·0	1·167	1626

(V = 310·0 c.c.; W = 0·1467 g.)

TABLE IV.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
25·1	361·4°	1·400	1576	41·5	408·8°	1·618	1467
30·2	367·7	1·480	1561	40·9	399·6	1·612	1487
39·8	385·4	1·600	1519	39·8	380·2	1·600	1531
40·6	395·8	1·609	1495	37·7	376·6	1·576	1539
41·1	405·7	1·614	1473	18·3	348·9	1·262	1608

(V = 579·7 c.c.; W = 0·4083 g.)

TABLE V.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
66·6	410·0°	1·823	1464	61·8	397·0°	1·791	1493
67·6	419·6	1·830	1444	55·6	392·2	1·745	1503
65·2	399·7	1·814	1487				

(V = 314·7 c.c.; W = 0·3575 g.)

TABLE VI.

p.	t.	$\log p$.	$1/T \cdot 10^6$.	p.	t.	$\log p$.	$1/T \cdot 10^6$.
64·5	397·2°	1·810	1492	88·7	436·1°	1·948	1410
79·7	406·8	1·901	1471	89·2	440·0	1·950	1403
85·3	415·9	1·931	1452	84·1	410·1	1·925	1464
87·0	426·5	1·940	1430				

(V = 314·0 c.c.; W = 0·4495 g.)

When the above values of $\log p$ and $1/T$ are plotted, a straight line is obtained for the points corresponding to saturated vapour which is cut by five other lines which correspond to the unsaturated vapour in the various experiments. From the points of intersection, the

temperature and pressure of the just-saturated vapour can be found accurately, and from these the vapour density is calculated from the formula

$$\text{Vapour density} = \tfrac{1}{2}M = \tfrac{1}{2} \times 22{,}400 \times 76WT/273Vp.$$

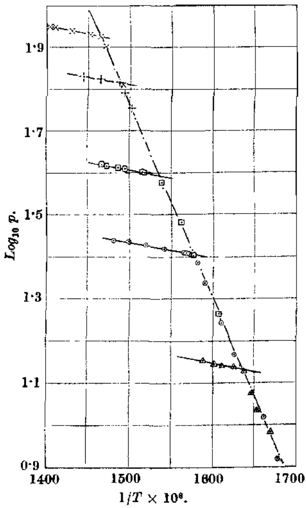
The values calculated from this formula are :

Experiment	II	III	IV	V	VI	
Vapour density	36·1	36·4	36·2	36·5	36·1.	Mean, 36·26.

Calc. for $NH_3 + HI$, 36·24.

The divergence of the results from the theoretical value required for complete dissociation is very small and within the limits of experimental error. It may consequently be concluded that up to 400° the vapour of ammonium iodide is always completely dissociated.

FIG. 2.



Points from Table II △, Table III ⊙, Table IV ▣, Table V +, Table VI ×.

It is of interest to note that no tendency was observed for the ammonium iodide to be adsorbed on the glass walls, as was the case with ammonium bromide. Near the point where the vapour becomes unsaturated there was always a tendency for the vapour pressures to be low owing to the slowness with which the last particles of salt evaporate. In spite of this and of the fact that rather rapid working was desirable at the higher temperatures, none of the points was more than a few mm. below the normal vapour-pressure line.

Since Q is not a temperature function we are justified in applying the well-known thermodynamical relationship, $d\log_e p/dT = Q/RT^2$, or $d\log_e p/d(1/T) = -Q/R$. From Fig. 2 we find that $\log_{10}p = -4616{\cdot}5.1/T + 8{\cdot}67$, and hence $Q/R =$

$4616 \cdot 5 \times 2 \cdot 303$, or $Q = 21 \cdot 1 \times 10^3$ cals. for $\frac{1}{2}$ g.-mol. of ammonium iodide. Hence the value per g.-mol. is $42 \cdot 2 \times 10^3$ cals., whereas Johnson obtained the value $43 \cdot 5 \times 10^3$ cals.

Summary.

The pressure and density of saturated ammonium iodide vapour have been redetermined, and it bas been shown that the vapour is completely dissociated at all temperatures up to 400°.

In conclusion, the authors wish to thank Professor Smits, in whose laboratory these experiments were carried out, for his kind interest in tbis work.

THE UNIVERSITY, AMSTERDAM.
THE ROYAL COLLEGE OF SCIENCE, LONDON.
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XLIII.—*Esters of Phosphoric Acid. Part I. Phosphates of Cetyl Alcohol, Cholesterol, Chloroethyl Alcohol, and Ethylene Glycol.*

By ROBERT HENRY ADERS PLIMMER and WILLIAM JOHN NOBBS BURCH.

CETYL dihydrogen phosphate (cetylphosphoric acid) has been described by Biehringer (*Ber.*, 1905, **38**, 3974) and cholesteryl phosphates have been prepared by Euler and Bernton (*Ber.*, 1927, **60**, 1720). The latter compounds had not been described when our work was started. Our object has been a study of not only the mono- but also the di- and tri-esters of cetyl alcohol and of cholesterol with phosphoric acid. Both these alcohols occur in nature as esters and their phosphates may likewise be present in animal or vegetable products.

Of the several methods of preparing esters of phosphoric acid the action of syrupy phosphoric acid, or phosphoric oxide, upon the alcohol has yielded the mono- or di-ester. Phosphoryl chloride and the alcohol yield intermediate compounds which are decomposed by water, giving the mono- and di-esters. By means of the sodium alcoholate a tri-ester was prepared by Limpricht (*Annalen*, 1865, **134**, 347). The tri-ester has been obtained from silver alkyl phosphate (Lossen and Kohler, *Annalen*, 1891, **262**, 195) and by the action of phosphorus pentachloride (Winssinger, *Bull. Soc. chim.*, 1888, **48**, 111).

The reaction between ethyl metaphosphate and alcohols was introduced by Langheld (*Ber.*, 1911, **44**, 2076). This method has been

specially studied and the products of the reaction are described in Part II (following paper).

It has been necessary to try all the methods above mentioned in order to obtain the mono-, di- and tri-esters of cetyl alcohol and of cholesterol with phosphoric acid.

Carré (*Compt. rend.*, 1904, **138**, 374) prepared the phosphoric esters of ethylene glycol by heating the glycol and phosphoric acid together in molecular proportion. He isolated the mono-ester, but was unable to separate the di- and tri-esters.

Since it was likely that a mixture of esters would always be obtained by the use of glycol, it was considered that a better method would be to start from ethylene chlorohydrin and then to convert the chloroethyl phosphoric esters into the corresponding β-hydroxyethyl compounds. Barium chloroethyl phosphate was prepared by Fischer (*Ber.*, 1920, **53**, 1620) by the action of phosphoryl chloride on glycol.

The three chloroethyl phosphates have been made by us by the action of phosphoryl chloride on ethylene chlorohydrin and they have been converted into the mono- and di-β-hydroxyethyl esters. The trichloroethyl ester was hydrolysed in the process and gave di-β-hydroxyethyl hydrogen phosphate. The monochloroethyl ester was also prepared by the action of ethyl metaphosphate on ethylene chlorohydrin. In order to prepare tri-β-hydroxyethyl phosphate the reaction of ethylene chlorohydrin with trisodium phosphate was attempted, but only the mono-ester resulted. The reaction of phosphoryl chloride with the sodium derivative of glycol was used to obtain more complex esters.

The hydrolysis of the di- and tri-esters by acid and by alkali has also been studied. It was shown by Plimmer (*Biochem. J.*, 1913, **7**, 72) that ethyl dihydrogen phosphate, glycerophosphoric acid, and phytic acid were hydrolysed by acid, but were stable to alkali. Phosphoproteins were found by Plimmer and Scott (J., 1908, **93**, 1699) to be easily hydrolysed by alkali. There appears to be no information about the hydrolysis of the di- and tri-esters.

EXPERIMENTAL.

Barium Monocetyl Phosphate and Monocetyl Dihydrogen Phosphate. —3·5 G. of phosphoryl chloride (1 mol.) were added slowly to a mechanically stirred solution of 5 g. of cetyl alcohol in chloroform. The mixture was warmed under reflux on a water-bath for 2 hours, kept for 24 hours, and then poured into water and thoroughly shaken in order to dissolve the oil. The solution was made neutral to phenolphthalein with barium carbonate and barium hydroxide, the barium phosphate removed, and the filtrate concentrated and treated

with an equal volume of alcohol. Crystals (5·5 g.) separated (yield, 60%). On recrystallisation from alcohol and water, pale yellow lustrous crystals of *barium monocetyl phosphate* were obtained (Found : H_2O, 4·4. Found in material dried at 110° : Ba, 29·8; P, 6·3.* $C_{16}H_{33}O_4PBa,H_2O$ requires H_2O, 3·7%. $C_{16}H_{33}O_4PBa$ requires Ba, 30·0; P, 6·8%).

Monocetyl dihydrogen phosphate was formed from the barium salt by the action of dilute sulphuric acid; it was obtained from the filtered concentrated solution. After crystallising from ether, it sintered at 61°, melted at 72°, and corresponded with the compound prepared by Biehringer (*loc. cit.*). The sodium salt, prepared by double decomposition with sodium sulphate, formed colourless crystals soluble in cold water.

Dicetylphosphoryl Chloride and Barium Dicetyl Phosphate.—A mixture of 9 g. of phosphoryl chloride and 25 g. of cetyl alcohol in chloroform was heated under reflux on a water-bath until hydrogen chloride ceased to be evolved. The solution was poured into a large excess of milk of lime and kept for 12 hours. The precipitate was filtered off and washed several times with water. Excess of lime was removed from the filtrate by means of carbon dioxide, and the filtered solution concentrated; 5 g. of a white crystalline powder, which consisted of *calcium monocetyl phosphate*, were obtained on evaporation (Found: Ca, 10·9; P, 8·7. $C_{16}H_{33}O_4PCa$ requires Ca, 11·1; P, 8·5%).

The precipitate was extracted with chloroform, and the chloroform solution evaporated to dryness. *Dicetylphosphoryl chloride* remained as a yellow powder, insoluble in water, soluble with difficulty in alcohol, and very easily soluble in chloroform (yield, 19 g. or 60%) [Found: C, 68·7; H, 11·7; Cl, 6·6; P, 6·0. $(C_{16}H_{33}O)_2POCl$ requires C, 68·1; H, 11·7; Cl, 6·3; P, 5·5%].

When dicetylphosphoryl chloride was boiled under reflux with excess of baryta solution for 10 hours, *barium dicetyl phosphate* formed as a yellowish grease on the surface; it solidified to a hard solid on cooling. It was washed with hot water to remove traces of barium monocetyl phosphate and recrystallised from aqueous alcohol [Found: Ba, 11·7; P, 4·7. $\{(C_{16}H_{33})_2PO_4\}_2Ba$ requires Ba, 11·2; P, 5·05%].

Owing to the insolubility of this salt and the readiness with which it is hydrolysed by acid, dicetyl hydrogen phosphate could not be prepared in a pure state. The acid softened at 64°.

In an attempt to obtain the intermediate cetylphosphoryl

* All the phosphorus analyses recorded in this paper were made by Neumann's method as modified by Plimmer and Bayliss (*J. Physiol.*, 1906, **33**, 439).

chlorides which are formed by the action of phosphoryl chloride upon the alcohol (compare Wichelhaus, *Annalen*, 1868, Suppl. Bd. 6, 257), cetyl alcohol and phosphoryl chloride in molecular proportion were heated under reflux on a water-bath for 6 hours, and the product fractionated in a vacuum. No compound could be separated other than cetene, b. p. 153°/15 mm. (compare Dumas and Peligot, *Ann. Chim. Phys.*, 1836, **62**, 8) (Found: C, 85·2; H, 14·8; *M*, ebullioscopic in alcohol, 230. Calc. for $C_{16}H_{32}$: C, 85·7; H, 14·3%; *M*, 224).

Tricetyl Phosphate.—5 G. of cetyl alcohol were heated on a water-bath, and 3 g. of phosphorus pentachloride added very gradually. The yellow waxy product was heated for 2 hours, shaken with several changes of hot water, dried in a vacuum, and crystallised from ligroin, soft, colourless, cubic crystals, m. p. 61°, very easily soluble in chloroform and benzene, being obtained [Found: C, 74·1; H, 12·3; P, 3·95. Calc. for $(C_{16}H_{33})_3PO_4$: C, 74·6; H, 12·85; P, 4·0%].

This compound was also obtained by boiling excess of cetyl alcohol with phosphoric oxide in presence of ether (Cavalier's method, *Ann. Chim. Phys.*, 1899, **18**, 499) in an attempt to prepare dicetyl hydrogen phosphate. To 15 g. of cetyl alcohol, dissolved in ether, 2·5 g. of phosphoric oxide were quickly added. The mixture was heated under reflux until no solid separated on cooling (about 7 days). The ether was removed by evaporation, and the residue crystallised from alcohol, a white crystalline solid, m. p. 61°, being obtained (Found: P, 3·9%). It gave sodium dicetyl phosphate on boiling with dilute caustic soda solution.

Barium Monocholesteryl Phosphate.—4·2 G. (1 mol.) of phosphoryl chloride were slowly added to a mechanically stirred solution of 12 g. of cholesterol in chloroform. After 24 hours the mixture, which had become red, was shaken with a large volume of water and kept for 24 hours. The water was separated and made neutral to phenolphthalein with barium carbonate and baryta. Barium phosphate was filtered off, and the filtrate concentrated and treated with an equal volume of alcohol. A gelatinous precipitate of barium cholesteryl phosphate, barium phosphate, and barium chloride was produced. Repeated crystallisation from aqueous alcohol gave a small yield of *barium monocholesteryl phosphate*, which crystallised in fine white platelets from alcohol and water (Found: H_2O, 10·8; P, 4·6; Ba, 20·15. $C_{27}H_{45}O_4PBa,4H_2O$ requires H_2O, 10·7; P, 4·6; Ba, 20·35%).

Monocholesteryl dihydrogen phosphate was prepared from this salt by precipitating the barium with sulphuric acid. The opalescent filtrate, which could not be clarified even on prolonged boiling, was

evaporated to dryness, and the residue crystallised from chloroform [Found: P, 6·5. $(C_{27}H_{45})H_2PO_4$ requires P, 6·6%].

The lead and silver salts are precipitated on addition of lead acetate and silver nitrate to solutions of the barium salt. The copper and sodium salts are soluble in water.

Barium Dicholesteryl Phosphate.—2 G. of phosphoryl chloride were added slowly to 8 g. of cholesterol dissolved in chloroform and the mixture was heated under reflux on a water-bath for 3 hours. The solution was kept for 24 hours and then shaken with a litre of water. The aqueous layer was separated from the cloudy chloroform layer (which contained cholesteryl ether and unchanged cholesterol), made neutral to phenolphthalein with barium carbonate and baryta, and concentrated on a water-bath. On addition of alcohol, barium monocholesteryl phosphate was precipitated. The filtrate was evaporated to dryness, and the residue extracted with 90% alcohol. The crystals which separated from the extract were recrystallised, a very small yield of white minute crystals of *barium dicholesteryl phosphate* being obtained [Found: Ba, 7·5; P, 3·4. $\{(C_{27}H_{45})_2PO_4\}_2Ba$ requires Ba, 7·5; P, 3·4%].

By exactly removing the barium with sulphuric acid and evaporating the filtrate to dryness, *dicholesteryl hydrogen phosphate* was obtained as a syrup which solidified in a vacuum desiccator after several days. The white crystalline magma was insoluble in alcohol but soluble in chloroform [Found: P, 3·7. $(C_{27}H_{45})_2HPO_4$ requires P, 3·7%].

Tricholesteryl Phosphate.—When a mixture of 2 g. of phosphorus pentachloride and 7·6 g. of cholesterol was gently warmed on a water-bath, a vigorous reaction took place and the mixture became liquid. On cooling, it set to a yellow solid, which was crystallised repeatedly from acetone. The ester, however, could not thus be entirely freed from cholesteryl chloride [Found: C, 78·1; H, 10·1; P, 2·4. $(C_{27}H_{45})_3PO_4$ requires C, 80·8; H, 11·2; P, 2·5%].

Investigation of Euler and Bernton's Compounds.—Since the above work was completed * the preparation of mono- and di-cholesteryl phosphates has been described by Euler and Bernton. For comparison with our compounds their experiments have been repeated.

(*a*) 3·86 G. of cholesterol, dissolved in 20 c.c. of pyridine, were cooled in a freezing mixture and poured into 6 g. of phosphoryl chloride in 25 c.c. of pyridine. After 12 hours, the mixture was poured into water and the slimy mass, which was filtered off with great difficulty, was dried in a vacuum desiccator and crystallised from

* A paper describing these compounds was read at a meeting of the Biochemical Society in June, 1925.

chloroform. The compound had m. p. 195° and contained phosphorus (6·64%) corresponding to monocholesteryl dihydrogen phosphate.

(*b*) Equivalent quantities of phosphoryl chloride and cholesterol were mixed in the reverse order, as also described by the authors, but we did not succeed in isolating a compound corresponding to dicholesteryl hydrogen phosphate. The product of the reaction in our experiments was a voluminous frothy mass from which dicholesteryl ether of m. p. 74° was isolated by extraction with 80% alcohol.

Barium β-Hydroxyethyl Phosphate and Tri-β-chloroethyl Phosphate.—15 G. of phosphoryl chloride were slowly added to 30 g. of ethylene chlorohydrin, which was mechanically stirred, and the mixture kept for 24 hours. It was then shaken with ten times its volume of water. *Tri-β-chloroethyl phosphate* separated as a heavy oil (3 c.c.), which was washed several times with water to remove hydrochloric acid and dried in a vacuum desiccator over caustic potash; it then had *d* 1·39 and b. p. 140°/40 mm. [Found: C, 24·3; H, 4·4; P, 10·8; Cl, 36·9. $(C_2H_4Cl)_3PO_4$ requires C, 25·2; H, 4·3; P, 10·9; Cl, 37·3%].

The aqueous solution was evaporated to dryness in a vacuum, the residue dissolved in water, and the solution made neutral to phenolphthalein with baryta and concentrated. On addition of alcohol, 12 g. of a mixture, probably of barium chloroethyl phosphate with barium chloroethyl pyrophosphate, crystallised. This was dissolved in water, the barium removed with sulphuric acid, and the solution boiled with excess of yellow lead oxide for 24 hours and filtered. Lead was then removed with hydrogen sulphide, and the solution evaporated in a vacuum and neutralised with baryta. The barium β-hydroxyethyl phosphate obtained on evaporation was recrystallised from aqueous alcohol (Found: Ba, 49·3; P, 10·6. Calc. for $HO·C_2H_4·O·PO_3Ba$: Ba, 49·4; P, 11·2%).

Barium Di-β-hydroxyethyl Phosphate.—The above procedure was repeated with 15 g. of phosphoryl chloride and 15 g. of ethylene chlorohydrin, but the mixture was heated on a water-bath for 2 hours. After treatment with water and separation of the oil, the aqueous solution was neutralised with baryta, concentrated, and boiled with excess of lead oxide, and finally the lead salts were converted into barium salts as described above. A mixture of mono- and di-β-hydroxyethyl phosphates was obtained. Separation was effected by crystallisation from water, the *barium* salt of the di-ester being the less soluble [Found: H_2O, 6·7; Ba, 25·55; P, 11·9. $(C_2H_4·OH)_2PO_4\}_2Ba,2H_2O$ requires H_2O, 6·6; Ba, 25·2; P, 11·4%].

Barium β-Chloroethyl Phosphate.—The barium salts of the chloro-

ethyl phosphates could not be isolated in a pure condition by the above method. Barium chloroethyl phosphate could not be obtained by Fischer's method, possibly owing to the great heat evolved in the reaction, though the reagents were maintained as far as possible at −20°. By substituting ethylene chlorohydrin for glycol a fair yield of the salt was obtained.

8·2 G. of ethylene chlorohydrin in 40 c.c. of pyridine cooled to −20° were added very slowly to 30·6 g. of phosphoryl chloride in 80 c.c. of pyridine kept below −15°. After remaining at this temperature for 2 hours, the mixture was poured into 2 litres of water containing ice, to which 120 c.c. of 25% sulphuric acid had been added. Hydrochloric acid was removed from the solution by means of silver carbonate, and the excess of silver by hydrogen sulphide, and the solution, after being freed from the latter reagent, was made neutral to phenolphthalein with baryta and evaporated in a vacuum until free from pyridine; the excess of barium was then precipitated by means of carbon dioxide. The filtrate from the barium carbonate was concentrated in a vacuum to 200 c.c., alcohol added, and the precipitated *barium chloroethyl phosphate* recrystallised from 50% alcohol (yield, 7 g.) [Found: H_2O, 5·7; Cl, 11·0; P, 9·6; Ba, 43·3. $(C_2H_4Cl)PO_4Ba,H_2O$ requires H_2O, 5·4; Cl, 11·2; P, 9·9; Ba, 43·7%].

The barium salt decomposes at 120°. For the further identification of monochloroethyl dihydrogen phosphate the *brucine* salt was found to be of most value. It is obtained by adding the calculated quantity of brucine to an aqueous solution of monochloroethyl dihydrogen phosphate. The brucine rapidly dissolves and the salt almost immediately begins to crystallise in tufts of fine needles (yield, almost theoretical). The salt is fairly readily soluble in hot water, but almost insoluble in cold [Found: H_2O, 13·5; P, 4·8; Cl, 5·8; N, 4·3; *M* (for anhydrous salt), ebullioscopic in alcohol, 564. $C_{23}H_{26}O_4N_2,(C_2H_4Cl)H_2PO_4,4H_2O$ requires H_2O, 11·3; P, 4·95; Cl, 5·7; N, 4·5%; *M* (for anhydrous salt), 554].

Conversion of Brucine β-Chloroethyl Phosphate into Barium β-Hydroxyethyl Phosphate.—The salt (6 g.) was dissolved in hot water, the brucine removed by ammonia, and the filtrate boiled with excess of yellow lead oxide. Lead was removed by hydrogen sulphide, the solution neutralised with baryta and evaporated in a vacuum, and alcohol added. The precipitated barium β-hydroxyethyl phosphate was recrystallised from aqueous alcohol (yield, nearly 2 g.) (Found: Ba, 49·7; P, 11·0%).

The Action of Ethyl Metaphosphate on Ethylene Chlorohydrin.—This reaction also was tried as a means of preparing barium monochloroethyl phosphate (see Part II).

A mixture of 16 g. of ethylene chlorohydrin and 11 g. of ethyl metaphosphate in chloroform was heated under reflux on a water-bath for 3 hours. The chloroform was then removed by distillation in a vacuum, and the residue dissolved in water and made neutral to phenolphthalein with baryta. The filtrate from barium phosphate was evaporated in a vacuum, and alcohol added very carefully until the solution became turbid. *Barium ethyl phosphate* separated on standing. After addition of rather more than an equal volume of alcohol to the filtrate, barium β-chloroethyl phosphate slowly separated. The salt was dissolved in water, the above separation repeated, and the barium chloroethyl phosphate recrystallised from 50% alcohol (yield, 3 g.) [Found: H_2O, 5·4. Found in salt dried at 110°: Cl, 12·3; P, 10·6; Ba, 45·8. Calc. for $(C_2H_4Cl)PO_4Ba,H_2O$: H_2O, 5·4. Calc. for $(C_2H_4Cl)PO_4Ba$: Cl, 12·0; P, 10·5; Ba, 46·4%]. It was converted into barium β-hydroxyethyl phosphate by boiling with yellow lead oxide as described above (Found: Ba, 50·8; P, 11·3%).

Formation of Barium Di-β-hydroxyethyl Phosphate from Trichloroethyl Phosphate.—5 G. of trichloroethyl phosphate were boiled with excess of yellow lead oxide and water for 24 hours. Lead was removed from the filtered solution by hydrogen sulphide, and the excess of the latter by evaporation in a vacuum. The solution was then neutralised with baryta and evaporated in a vacuum. Barium di-β-hydroxyethyl phosphate (3 g.) separated and was recrystallised (Found: H_2O, 5·5; Ba, 23·9; P, 11·9%).

Since the trichloroethyl ester suffered hydrolysis by this treatment, its conversion into trihydroxyethyl phosphate was attempted by the action of moist silver oxide. The syrupy trichloroethyl ester, on being left in contact with silver oxide for 8 weeks, was changed into a mobile liquid. This was evaporated in a vacuum. White feathery crystals of silver di-β-hydroxyethyl phosphate were obtained. As this salt was very soluble in water, it was converted into the barium salt by successive treatment with hydrogen sulphide and baryta (Found: Ba, 26·7; P, 12·0%).

Formation of Disodium β-Hydroxyethyl Phosphate from Ethylene Chlorohydrin and Trisodium Phosphate.—This reaction was tried as a means of preparing tri-β-hydroxyethyl phosphate. 10 G. of ethylene chlorohydrin were added to a saturated solution of 20 g. of trisodium phosphate. A sheen, due to minute crystals, appeared almost at once in the solution and developed into a heavy white precipitate. Just sufficient water was added to dissolve the crystals and alcohol was added until the solution was turbid. Tiny glistening platelets of *disodium β-hydroxyethyl phosphate* were first formed and afterwards

sodium phosphate crystallised. The crystals were separated by fractional crystallisation from aqueous alcohol and finally disodium β-hydroxyethyl phosphate (11 g.) was obtained in large transparent plates, m. p. 61° [Found: H_2O, 37·1; Na, 15·5; P, 10·4. $(C_2H_4\cdot OH)PO_4Na_2,6H_2O$ requires H_2O, 36·7; Na, 15·6; P, 10·5%].

Formation of Sodium Ethylene Phosphate.—Besides the above esters of ethylene glycol and phosphoric acid, several other esters are theoretically capable of existence, such as $\begin{matrix}CH_2\cdot O\\ CH_2\cdot O\end{matrix}\!>\!PO\cdot OH$. An attempt was made to prepare a salt of this compound as follows.

The disodium derivative (18 g.) of ethylene glycol (made by heating the glycol with excess of sodium at 170°) was suspended in 500 c.c. of dry chloroform and 28 g. of phosphoryl chloride were slowly added. Much heat was evolved and the apparatus had to be cooled. After the addition the mixture was warmed on a water-bath. Some greasy material, which was probably the excess of the disodium derivative, separated on the surface. The rest was shaken with water and separated from the chloroform, which contained only a trace of trichloroethyl phosphate. The aqueous solution was neutralised with baryta and evaporated in a vacuum. Sodium chloride crystallised. On evaporation of the mother-liquor in a vacuum over sulphuric acid, a colourless syrup resulted containing a mass of regular, truncated, octahedral crystals. These crystals could not be separated, as they formed only when the syrup was too viscid to filter, and it has been so far impossible to find a solvent which did not dissolve both crystals and syrup and prevent crystallisation. The great solubility of the crystals is so different from that of the salts of hydroxyethyl phosphates that it is probable that they are the salt of the above ethylene hydrogen phosphate.

Hydrolysis of the Esters.

Hydrolysis of Barium Diethyl Phosphate and of Triethyl Phosphate.—In view of the fact that ethyl dihydrogen phosphate is not hydrolysed by alkali, the examination of the hydrolysis of the diethyl and triethyl esters necessitates estimation of alcohol, since inorganic phosphoric acid will not be formed. The methods of Haggard (*J. Biol. Chem.*, 1923, **55**, 132) and of Shaffer and Ronzoni (*ibid.*, 1923, **57**, 741) for the estimation of ether in blood and other fluids seemed capable of adaptation to the determination of alcohol.

(1) *Haggard's method.* This consists in the oxidation of the ether, which is removed by a current of air from the liquid, by iodine

pentoxide. The liberated iodine is absorbed in potassium iodide solution and titrated with thiosulphate.

On testing the method with alcohol it was found that the reaction

$$5C_2H_5{\cdot}OH + 6I_2O_5 = 15H_2O + 10CO_2 + 6I_2$$

takes place at 200°.

The experiment was carried out by bubbling dry air very slowly through the alcohol solution and then through a U tube (in an oil-bath at 200°) containing alternate layers of iodine pentoxide (40 g.) and glass wool. The air current was then passed into potassium iodide solution to absorb the iodine. (Before use, the charged U tube had to be conditioned by heating it at 220° for about 10 hours until iodine was no longer evolved.) Alcohol was completely removed from the solution in 30 minutes, but the apparatus was not capable of dealing with more than 10 mg. of alcohol.

(2) *Shaffer and Ronzoni's method.* In this method the ether is separated by aeration and passed through a series of absorption bottles each containing 25 c.c. of 0·5*N*-potassium dichromate in 50% sulphuric acid. The unreduced dichromate is then estimated by means of potassium iodide and thiosulphate.

It was found that the alcohol could be removed by aeration if the solution were heated on a water-bath. It was oxidised to acetic acid by the dichromate and not further, but at the end of the experiment it was necessary to boil the dichromate for a few minutes to complete the oxidation. The results obtained by this method with pure alcohol were accurate to within 0·5%.

The second method, which is much simpler than the first, was used in the experiments with ethyl and propyl phosphates.

Hydrolysis. 1 G. portions of barium diethyl and of triethyl phosphate were heated under reflux with 200 c.c. of 2*N*-sodium hydroxide on a water-bath for periods ranging from 8 to 360 hours. The solution was then aerated and the alcohol drawn through a train of three absorption bottles each containing 25 c.c. of 0·5*N*-potassium dichromate made up with 50% sulphuric acid. The dichromate portions were mixed, boiled for a few minutes, and made up to a volume of 250 c.c. Quantities of 25 c.c. were treated with excess of potassium iodide solution, and the liberated iodine estimated with thiosulphate.

The acid hydrolysis was carried out in the same way, 200 c.c. of 2*N*-sulphuric acid being used.

In a blank experiment 75 c.c. of the dichromate solution, as used for absorption of the alcohol, were equivalent to 370 c.c. of 0·1*N*-thiosulphate. The results, including those for barium dipropyl phosphate, were as follows :

Alkaline Hydrolysis at 90°.

Phosphate.	Quantity taken (g).	Time (hours).	Alcohol oxidised (as c.c. of 0·1*N*-thiosulphate).	Mols. of alcohol removed.
Barium diethyl	1·0	8	No hydrolysis	0
	1·0	24	,,	0
	1·0	96	,,	0
Barium dipropyl	1·0	48	,,	0
	1·0	96	,,	0
Triethyl	1·0303	15	178	0·79
	1·0303	30	208	0·92

Acid Hydrolysis at 90°.

Phosphate.	Quantity taken (g).	Time (hours).	Alcohol oxidised (as c.c. of 0·1*N*-thiosulphate).	Mols. of alcohol removed.
Barium diethyl	1·0	20	8·2	0·045
	1·0	48	15	0·086
	1·0	144	103	0·53
	1·0	216	148	0·82
	1·0	386	337·5	1·87
Barium dipropyl	1·0	48	44	0·275
	1·0	96	84	0·525
Triethyl	1·0	8	190	0·84
	1·0	48	253	1·12
	1·0	120	315	1·4
	1·0	240	405	1·8
	1·0	360	563	2·5

The dialkyl phosphates are thus not hydrolysed by alkali, and slowly by acid with complete removal of the alcohol only after a long time. Triethyl phosphate was converted into the diethyl phosphate by alkali and almost completely hydrolysed by acid after 360 hours.

Hydrolysis of the Cetyl Phosphates.—The extent of hydrolysis of these esters could be determined by weighing the cetyl alcohol extracted, after cooling, by ether.

Alkaline hydrolysis. 1 G. portions of the barium salts of the mono- and di-cetyl phosphates were boiled under reflux with 200 c.c. of 2*N*-sodium hydroxide: there was no separation of cetyl alcohol.

1 G. of tricetyl phosphate was boiled with 200 c.c. of *N*-sodium hydroxide for 2 hours. A white curdy mass which formed on the surface of the liquid was filtered off; ether then extracted 0·31 g. of cetyl alcohol from the liquid. The aqueous solution on cooling deposited a white flocculent precipitate of *sodium dicetyl phosphate*, which was washed with ether to remove cetyl alcohol (Found: P, 5·3. $(C_{16}H_{33})_2PO_4Na$ requires P, 5·45%).

Acid hydrolysis. 1 G. portions of barium mono- and di-cetyl phosphates were boiled under reflux with 200 c.c. of 2*N*-sulphuric acid for 8 hours in each case. The mono-ester gave 0·509 g. of cetyl alcohol (0·96 mol.), and the di-ester 0·722 g. (1·83 mols.). The results are similar to those obtained with ethyl and propyl phosphates.

Hydrolysis of Phenyl Phosphates.—The barium salts of mono- and di-phenyl hydrogen phosphates were prepared by the action of

phosphoryl chloride on phenol. Molecular quantities were heated in an oil-bath at 110° for about 10 hours and the product was fractionated in a vacuum to obtain the corresponding phosphoryl chloride compounds. Monophenylphosphoryl chloride, $OPh \cdot POCl_2$, distilled at 240°/ 760 mm., and diphenylphosphoryl chloride, $(OPh)_2POCl$, at 212—215°/21 mm. These compounds were hydrolysed to the phosphoric esters by shaking with water at 60°. The solutions were filtered, and the filtrates evaporated in a vacuum desiccator containing sodium hydroxide.

Triphenyl phosphate was prepared by the action of phosphorus pentachloride on phenol.

The esters were hydrolysed by heating about 1 g. quantities with 200 c.c. of *N*-hydrochloric acid or 200 c.c. of *N*-sodium hydroxide.

The extent of the hydrolysis of these esters was ascertained in the case of the mono-ester by precipitation of the inorganic phosphoric acid as ammonium magnesium phosphate and conversion into magnesium pyrophosphate, and in the case of the di- and tri-esters by steam distillation (after acidification with acetic acid in the alkaline hydrolysis) and estimation of the phenol by bromination in an aliquot part of the distillate, which was made up to 500 c.c. The bromination was effected in a stoppered bottle by adding 10 c.c. of 0·5*N*-potassium bromate and 10 c.c. of 0·5*N*-potassium bromide and 5 c.c. of concentrated hydrochloric acid. After 15 minutes, excess of potassium iodide was added and the iodine liberated was titrated with thiosulphate. 10 C.c. of the bromate solution were equivalent to 32·8 c.c. of 0·1*N*-thiosulphate.

The results of the hydrolysis were as follows :

Acid Hydrolysis at 85°.

Ester.	Quantity taken (g.).	Time (hours).	C.c. of thiosulphate.	Mols. of phenol removed.
Triphenyl	1·0222	144	283·3	1·95
Diphenyl	0·9994	24	37·25	0·20
	0·9907	76	141·5	1·01
			($Mg_2P_2O_7$)	
Monophenyl	1·0059	48	0·2377 g.	0·37
	1·0	168	0·4698 g.	0·73

Alkaline Hydrolysis at 85°.

Ester.	Quantity taken (g.).	Time (hours).	C.c. of thiosulphate.	Mols. of phenol removed.
Triphenyl	1·0061	72	268 c.c.	1·9
	1·0058	170	430	3·0
Diphenyl	1·0061	70	280	1·5
	1·0022	170	366	1·98
Monophenyl	1·00	24	194	0·7
	1·00	48	250·5	0·9
	1·00	72	261	0·98

The hydrolysis of mono- and di-phenyl phosphates by alkalis was also examined at 40°, both the inorganic phosphoric acid and the phenol being estimated :

Diphenyl: 1·0037 g. in 24 hours gave 0·16 g. $Mg_2P_2O_7$ and 1·36 mols. phenol.
Monophenyl: 1·0051 g. in 24 hours gave 0·2232 g. $Mg_2P_2O_7$ and 0·35 mol. phenol.

The hydrolysis was thus quite appreciable. This difference between the aliphatic alcohols and phenol may be due to the acidic character of the hydroxyl group conferred upon it by the electronegative nature of the benzene nucleus.

Summary.

Mono-, di-, and tri-cetyl phosphates have been prepared by the action of phosphoryl chloride and pentachloride upon cetyl alcohol. The first two esters were isolated as barium salts.

Mono-, di-, and tri-cholesteryl phosphates have been prepared by similar methods. Tricholesteryl phosphate was not prepared in a pure condition.

Mono- and di-β-chloroethyl phosphates (isolated as barium salts) and trichloroethyl phosphate have been prepared by the action of phosphoryl chloride upon ethylene chlorohydrin.

Monochloroethyl phosphate has also been made by the action of ethyl metaphosphate upon ethylene chlorohydrin.

The barium salts of the mono- and di-chloroethyl phosphates have been converted into the barium salts of mono- and di-β-hydroxyethyl phosphates. Trichloroethyl phosphate was converted into a salt of di-β-hydroxyethyl phosphate.

Disodium β-hydroxyethyl phosphate was formed by the action of ethylene chlorohydrin upon trisodium phosphate.

A very soluble salt, probably of ethylene hydrogen phosphate, is formed by the action of phosphoryl chloride upon the disodium derivative of ethylene glycol. It could not be isolated.

The various esters of phosphoric acid can be completely hydrolysed by dilute acid.

The mono- and di-esters of the aliphatic alcohols with phosphoric acid are not hydrolysed, and the tri-ester is hydrolysed to the di-ester, by dilute alkali.

The mono-, di-, and tri-esters of phenol with phosphoric acid can be completely hydrolysed by dilute alkali.

ST. THOMAS'S HOSPITAL MEDICAL SCHOOL.
WESTMINSTER SCHOOL.
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XLIV.—*Esters of Phosphoric Acid. Part II. The Action of Ethyl Metaphosphate on Alcohols, Ammonia, and Some Amino-compounds.*

By Robert Henry Aders Plimmer and William John Nobbs Burch.

The action of ethyl metaphosphate on alcohols as a method of preparing esters of phosphoric acid was introduced by Langheld (*Ber.*, 1910, **43**, 1857; 1911, **44**, 2076), who claimed to have made several esters of natural origin but gave no data. The reaction was believed to take place in two stages. The ethyl metaphosphate first reacted with the alcohol by addition :

$$O_2P{\cdot}OEt + ROH = OP(OH)(OEt){\cdot}OR$$

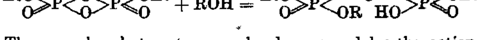
Then, at the temperature of the water-bath, the mono-ester and a mixed ether were produced. These products were believed to result either from the reaction

$$OP(OH)(OEt){\cdot}OR + ROH = OP(OH)_2{\cdot}OR + EtOR$$

or from

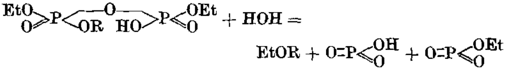
$$(a)\ O_2P{\cdot}OEt + ROH = O_2P{\cdot}OH + EtOR$$
$$(b)\ O_2P{\cdot}OH + ROH = OP(OH)_2{\cdot}OR.$$

No mixed phosphoric ester was apparently formed, nor were pyrophosphoric esters isolated; possibly they were not formed. In view of the uncertainty of the reaction and for the purpose of preparing certain esters of phosphoric acid, the method has now been tried with propyl alcohol, cetyl alcohol, phenol, and cholesterol, as well as with ethyl alcohol employed by Langheld. We have found that in most cases a mixed ether and sometimes a simple ether is produced and that, except in the case of cholesterol, there is always formed a mixture of the mono- and di-ester of the alcohol taken together with mono- and di-ethyl phosphates. It is difficult to explain the course of the reaction, but it appears that there are several stages. If ethyl metaphosphate has the double formula, as shown by molecular-weight determination, the first stage is probably the addition of the alcohol to form a pyrophosphate ester :



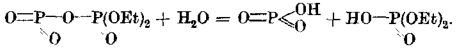
The pyrophosphate ester may be decomposed by the action of

water into a mixed ether, metaphosphoric acid, and ethyl metaphosphate :



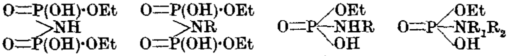
Finally, the metaphosphoric acid reacts with the alcohol to form the mono- and di-esters, $OP(OH)_2{\cdot}OR$ and $OP(OR)_2{\cdot}OH$. The simple ether may arise from the action of the alcohol (cetyl) upon the mono-ester (monocetyl).

By these reactions it is impossible to explain the formation of diethyl hydrogen phosphate in all cases. We venture to suggest that ethyl metaphosphate has an alternative formula and that it is decomposed by water into diethyl hydrogen phosphate and metaphosphoric acid :



This would agree with Langheld's observation (*Ber.*, 1910, **43**, 1859) that the solution coagulates albumin.

By the action of ethyl metaphosphate on ammonia and various amino-compounds, Langheld also prepared compounds to which he ascribed the formulæ I—IV.



(I.) (II.) (III.) (IV.)

Ammonia and primary amines formed iminopyrophosphates (I and II), secondary amines formed amino-orthophosphates (III and IV). They were decomposed by alkalis or water into ammonia or the amine. In a similar way Strecker and Heuser (*Ber.*, 1924, **57**, 1364) prepared compounds of ethyl metaphosphate with hydrazine, hydroxylamine, and phenylhydrazine. They assigned to them the composition ethyl hydrazino-orthophosphate,

$$O{:}P(OH)(OEt)(NH{\cdot}NH_2),$$

ethyl phenylhydrazino-orthophosphate, $O{:}P(OH)(OEt)(NH{\cdot}NHPh)$, and ethyl hydroxylamino-orthophosphate, $O{:}P(OH)(OEt)(NH{\cdot}OH)$. In all these compounds the nitrogen atom was believed to be directly attached to the phosphorus atom.

On account of the possible relation of these compounds to phosphoproteins in which phosphorus is combined with an amino-acid in a form easily hydrolysed by alkali (Plimmer and Bayliss, *J. Physiol.*, 1906, **33**, 439; Plimmer and Scott, J., 1908, **93**, 1699) it was thought

that further investigation of these compounds was of importance in the study of the combination of phosphorus in the phosphoproteins. We have found that these compounds after treatment with water give salts of ethyl dihydrogen phosphate with ammonia, hydrazine, or other amino-compounds.

EXPERIMENTAL.

Preparation of Ethyl Metaphosphate.—The ester was prepared as described by Langheld. From 200 g. of phosphoric oxide we obtained, after purification, 100 g. of ethyl metaphosphate as a heavy yellow syrup, which was kept in a vacuum desiccator [Found : C, 21·9; H, 4·6; P, 28·8; *M*, ebullioscopic in chloroform, 216·6, 214·6. Calc. for $EtPO_3$: C, 22·2; H, 4·6; P, 28·7%. $(EtPO_3)_2$ requires *M*, 216].

Ethyl metaphosphate is very soluble in chloroform and glacial acetic acid, moderately easily soluble in acetone, and very slightly soluble in ether, benzene, and ligroin.

Ethyl Alcohol and Ethyl Metaphosphate.—Ten g. of ethyl metaphosphate dissolved in chloroform were added to excess of absolute alcohol and heated under reflux on a water-bath for 2 hours; the mixture then gave no mistiness on addition of ether. The chloroform and excess of alcohol were distilled in a vacuum, the residue was dissolved in water, and the solution made neutral to phenolphthalein with barium carbonate and baryta and warmed on the water-bath. Alcohol was added until the first sign of turbidity appeared. *Barium ethyl phosphate* slowly crystallised in characteristic shining plates. It was recrystallised from aqueous alcohol (yield, 10·9 g.) (Found: H_2O, 5·6; P, 11·1.* $C_2H_5PO_4Ba,H_2O$ requires H_2O, 6·45; P, 11·1%).

The filtrate was divided into two equal parts. One part was evaporated to dryness; alcohol (80%) extracted from the residue *barium diethyl phosphate*, which was crystallised from 80% alcohol (yield, 4·5 g.) [Found: P, 14·0. $\{(C_2H_5)_2PO_4\}_2Ba$ requires P, 14·0%]. The second part was distilled in a vacuum, but no triethyl phosphate could be obtained.

The original distillate of chloroform and alcohol was not examined for the presence of ethyl ether.

Propyl Alcohol and Ethyl Metaphosphate.—A solution of 12 g. of *n*-propyl alcohol in chloroform was boiled under reflux with 11 g. of ethyl metaphosphate until it gave no mistiness on addition of ether. The chloroform was then distilled off in a vacuum, and the residue dissolved in ether and shaken with baryta solution to convert the

* The phosphorus analyses were made by the method of Neumann as modified by Plimmer and Bayliss (*J. Physiol.*, 1906, **33**, 439).

ester into its barium salt. The aqueous solution was evaporated to a small bulk in a vacuum, and alcohol added until the first sign of turbidity appeared; barium ethyl phosphate slowly crystallised (Found: H_2O, 6·0; P, 11·0%). The filtrate was evaporated to dryness in a vacuum; boiling alcohol extracted from the residue *barium di-n-propyl phosphate*, which crystallised on cooling (9 g.) and was recrystallised from hot alcohol [Found: Ba, 27·05; P, 12·4. $\{(C_3H_7)_2PO_4\}_2Ba$ requires Ba, 27·3; P, 12·45%]. From the remaining solid, 80% alcohol extracted barium diethyl phosphate (11 g.), which was recrystallised (Found: P, 14·0%). The impure *barium dipropyl pyrophosphate* that remained [Found: Ba, 36·7; P, 16·0. $(C_3H_7)_2P_2O_7Ba$ requires Ba, 34·5; P, 15·6%] was converted, by warming with dilute baryta solution, into *barium propyl phosphate* (Found: Ba, 49·9; P, 11·2. $C_3H_7PO_4Ba$ requires Ba, 49·8; P, 11·3%).

On redistilling the chloroform fraction at ordinary pressure, about 2 c.c. of a liquid boiling at 90° were obtained, presumably consisting of dipropyl ether. Ethyl propyl ether was not separable from the chloroform owing to the closeness of their boiling points.

Cetyl Alcohol and Ethyl Metaphosphate.—A solution of 10 g. of cetyl alcohol and 5 g. of ethyl metaphosphate in chloroform was heated under reflux for 2 hours, the chloroform was then evaporated in a vacuum and the residue was dissolved in ether and well shaken with a large volume of water. The aqueous solution was made neutral to phenolphthalein with concentrated baryta solution. From the precipitated barium mono- and di-cetyl phosphates, by repeated extraction with hot water, 2 g. of barium cetyl phosphate were separated; this was recrystallised from water (Found in material dried at 110°: Ba, 30·2; P, 7·0. Calc. for $C_{16}H_{33}PO_4Ba$: Ba, 30·0; P, 6·8%). The residue of barium dicetyl phosphate was dissolved in alcohol, filtered from barium phosphate, and precipitated, by addition of water, as a gelatinous mass which became a white powder (7 g.) on drying at 110° [Found: Ba, 11·6; P, 5·5. Calc. for $\{(C_{16}H_{33})_2PO_4\}_2Ba$: Ba, 11·17; P, 5·05%].

The filtrate from the precipitate of the cetyl phosphates was concentrated in a vacuum, and alcohol added; barium ethyl phosphate was precipitated (Found: P, 11·2%). On evaporating the filtrate to dryness and extracting the residue with 80% alcohol, barium diethyl phosphate (3 g.) was obtained; it was recrystallised from alcohol and water (Found: P, 13·7%).

The ethereal solution, fractionated under ordinary pressure, gave two fractions, b. p. 180° and 286° respectively. The former solidified after some time to a white wax, m. p. 20°, which was apparently ethyl cetyl ether (Found: C, 79·1; H, 13·75. Calc. for

$C_2H_5 \cdot O \cdot C_{16}H_{33}$: C, 80·0; H, 14·1%). (Cetyl alcohol melts at 50° and boils at 190°.) The other fraction was a pale yellow solid, m. p. 55°, presumably dicetyl ether.

Phenol and Ethyl Metaphosphate.—Phenol (5 g.) was treated with ethyl metaphosphate (5 g.) as described in the case of propyl alcohol. From the aqueous solution of barium salts, on addition of alcohol, barium ethyl phosphate (Found : P, 11·0%) and *barium phenyl phosphate* (Found in material dried at 110° : Ba, 43·2; P, 10·3. $C_6H_5PO_4Ba$ requires Ba, 44·2; P, 10·0%) were precipitated. They were separated by fractional crystallisation from aqueous alcohol, barium ethyl phosphate being the less soluble.

The filtrate was evaporated to dryness, and the residue extracted with absolute alcohol. Barium diethyl phosphate was insoluble and was recrystallised from dilute alcohol (Found : P, 14·1%). *Barium diphenyl phosphate* was obtained on evaporation of the alcoholic extract; it crystallised from 50% alcohol in fine needles [Found : loss at 60°, 10·15. $\{(C_6H_5)_2PO_4\}_2Ba,4H_2O$ requires loss, 10·4%. Found in anhydrous salt: Ba, 21·6; P, 9·8. $\{(C_6H_5)_2PO_4\}_2Ba$ requires Ba, 21·4; P, 9·7%]. The chloroform on fractionation gave phenetole, b. p. 176°.

Cholesterol and Ethyl Metaphosphate.—Cholesterol (3·25 g.) was treated with ethyl metaphosphate (5 g.) as in the case of cetyl alcohol (3 hours' heating). The neutralised aqueous solution of barium salts, after addition of alcohol, slowly deposited a mixture of barium ethyl phospbate (Found : P, 11·3%) and *barium cholesteryl phosphate.* They were separated by fractional crystallisation from aqueous alcohol. Only 0·5 g. of barium monocholesteryl phosphate was obtained (Found : loss at 110°, 10·8. $C_{27}H_{45}PO_4Ba,4H_2O$ requires loss, 10·6%. Found in anhydrous salt : Ba, 22·6; P, 5·1. $C_{27}H_{45}PO_4Ba$ requires Ba, 22·8; P, 5·15%). Barium dicholesteryl phosphate could not be obtained from the filtrate.

On fractionating the chloroform a brown oil (1 c.c.), b. p. 237°/20 mm., was obtained. This appeared to be *cholesteryl ethyl ether* (Found : C, 84·9; H, 12·1. $C_{27}H_{45} \cdot O \cdot C_2H_5$ requires C, 84·05; H, 12·1%). Dicholesteryl ether was not isolated.

Tyrosine and Ethyl Metaphosphate.—1 G. of tyrosine and 5 g. of ethyl metaphosphate were heated in dry chloroform under reflux on a water-bath for 3 hours. A colourless syrup which floated to the surface was found to contain a high percentage of phosphorus and a very low percentage of nitrogen. It seemed, therefore, that the tyrosine had merely dissolved, since on neutralisation with baryta it was precipitated.

The Product of the Reaction of Ethyl Metaphosphate with Ammonia.—Dry ammonia was passed into a solution of 10 g. of pure

ethyl metaphosphate in chloroform until the reaction was complete. A gelatinous mass was formed. The chloroform was removed by distillation in a vacuum, and the vitreous residue dissolved in dry alcohol and precipitated with dry ether (Found : C, 17·15; H, 6·7; P, 21·6%).

(*a*) 0·69 G. of the product was dissolved in water, 1 g. of sodium carbonate added, and air aspirated through the solution according to the method of Folin. Ammonia equivalent to 37 c.c. of 0·1*N*-acid was absorbed in excess of standard acid. Hence nitrogen (as ammonia) = 9·1%.

(*b*) 5 C.c. of a 0·69% solution of the product, when tested for amino-nitrogen by the Van Slyke method with acetic acid (Plimmer, J., 1925, **127**, 2651), gave 7·3 c.c. at 18° and 771 mm. after 24 hours. Allowance being made for the nitrogen in the blank determination, the amount of nitrogen = 4·2574 mg. Hence nitrogen = 10·8%.

These analyses and reactions correspond to those of ammonium ethyl hydrogen phosphate [$NH_4(C_2H_5)HPO_4$ requires N, 9·7; C, 16·7; H, 7·0; P, 21·7%], and not to those of an iminophosphate (Langheld, *loc. cit.*). A record of only one ammonium salt, $NH_4(C_2H_5)HPO_4$, could be found (Cavalier, *Ann. Chim. Phys.*, 1899, **18**, 449).

Diammonium ethyl phosphate was made from 10 g. of barium ethyl phosphate by adding 4·7 g. of ammonium sulphate in aqueous solution. The barium sulphate was removed, and the filtrate evaporated in a vacuum. A white crystalline salt was obtained which was very soluble in water [Found : N (as ammonia), 17·4; P, 19·1. $(NH_4)_2C_2H_5PO_4$ requires N, 17·5; P, 19·4%].

Ammonium Ethyl Hydrogen Phosphate.—A mixture of 20 g. of phosphoric oxide and 25 g. of alcohol in ether cooled in ice was left for 12 hours. It was then warmed at 40° for 2 hours, poured into water, and divided into two portions. One portion was partly neutralised with ammonia until the B.D.H. universal indicator used was yellow. The solution was then evaporated to a small bulk and left in a vacuum desiccator. After a time it became a vitreous mass and finally crystallised. The salt was very deliquescent and resembled the salt formed from ethyl metaphosphate and ammonia [Found : N (as ammonia), 9·5; P, 21·7%].

The other portion of the solution was treated with double the quantity of ammonia used above. White flaky crystals of diammonium ethyl phosphate separated [Found : N (as ammonia), 17·25; N (by Kjeldahl's method), 17·1; C, 15·05; H, 8·6; P, 20·4. $(NH_4)_2C_2H_5PO_4$ requires N, 17·5; C, 15·0; H, 8·1; P, 19·4%].

Ammonium diethyl phosphate was obtained as colourless deliquescent crystals from 1·32 g. of ammonium sulphate and 4·43 g. of

barium diethyl phosphate by removing the barium sulphate and concentrating the filtrate in a vacuum [Found : N (as ammonia), 7·9; P, 17·6. $NH_4(C_2H_5)_2PO_4$ requires N, 8·2; P, 18·1%].

The Product of the Reaction of Ethyl Metaphosphate with Hydrazine.—This product was prepared by the method of Strecker and Heuser (*loc. cit.*). It consisted of a pale yellow syrup (Found : P, 18·8%) and was tested as follows :—(*a*) 5 C.c. of a solution containing 0·4136 g. were shaken with benzaldehyde. The benzylideneazine formed gradually became crystalline (0·22 g.); m. p. 91°.

(*b*) On adding sodium carbonate solution and copper sulphate to a solution of the compound, there was a brisk effervescence of nitrogen and cuprous oxide was precipitated.

(*c*) On adding excess of copper sulphate to a solution of the compound a fine blue crystalline powder was precipitated [Found : Cu, 21·3; N, 9·8; SO_4, 66·1. $CuSO_4,(N_2H_4)H_2SO_4$ requires Cu, 21·7; N, 9·7; SO_4, 66·4%]. This powder was insoluble in water, and on addition of an alkali cuprous oxide was precipitated and nitrogen evolved. It contained neither phosphorus nor water, and the filtrate contained no hydrazine but the whole of the phosphorus of the compound.

The compound thus appears to be *hydrazine ethyl dihydrogen phosphate.* It reacts with copper sulphate to give *hydrazine copper sulphate* and copper ethyl phosphate :

$$N_2H_4(C_2H_5)H_2PO_4+2CuSO_4=(N_2H_4)H_2SO_4,CuSO_4+Cu(C_2H_5)PO_4.$$

The Product of the Reaction of Ethyl Metaphosphate with Phenylhydrazine.—This product was prepared by the method described by Strecker and Heuser (*loc. cit.*) and purified by repeated crystallisation from alcohol. It was tested as follows : (*a*) A solution of the compound in water containing sodium carbonate reduced copper sulphate in the cold.

(*b*) A solution of the compound was treated with barium carbonate; barium ethyl phosphate (Found : P, 10·8%) was obtained from the filtrate on addition of alcohol.

(*c*) The compound was kept for 24 hours with sodium carbonate solution in a stoppered bottle. The liquid then had a distinct odour of phenylhydrazine, and this base was extracted from it with ether and identified. On shaking a solution of the compound in water with benzaldehyde, benzaldehydephenylhydrazone, m. p. 152°, was isolated.

These reactions show clearly that the compound is a salt of phenylhydrazine with ethyl dihydrogen phosphate.

The Product of the Reaction of Ethyl Metaphosphate with Alanine.—Ten g. of alanine were boiled on a water-bath with an excess of ethyl

metaphosphate dissolved in dry chloroform. After 10 hours all the alanine had disappeared and a syrup separated on the surface. This was separated from the chloroform and evaporated in a vacuum. Yield, 16·9 g. The analytical figures (Found: N, 4·15; P, 20·9%) correspond fairly well to those required for alanine ethyl pyrophosphate, *viz.*, N, 4·3; P, 19·1%. The high percentage of phosphorus is probably due to the presence of ethyl dihydrogen phosphate.

The product was tested as follows: (*a*) Copper carbonate was added to the solution. The filtrate from the excess gave a mixture of the copper salt of alanine and copper ethyl phosphate. Their complete separation was not successful on account of the great solubility of both salts.

(*b*) Benzoyl chloride (5 g.) was added gradually to 4 g. of the product, the solution being kept alkaline with sodium carbonate. A mixture of benzoic acid and benzoylalanine was obtained. The benzoic acid was separated by solution in ligroin; the residue, crystallised from hot water, consisted of benzoylalanine, m. p. 162°, and contained no trace of phosphorus.

The product thus seems to be a salt of alanine with ethyl trihydrogen pyrophosphate, which becomes a salt of ethyl dihydrogen phosphate on treatment with water.

The Product of the Reaction of Ethyl Metaphosphate with Guanidine.—This reaction with the strongly basic guanidine was studied as a preliminary to the attempted preparation of a phosphorus derivative of arginine and of creatine. The latter combination has recently been described as occurring in muscle by Fiske and Subbarow (*Science*, 1928, **67**, 169).

Excess of ethyl metaphosphate dissolved in dry chloroform was boiled under reflux with 5 g. of guanidine carbonate for 20 hours. The guanidine went into solution and a syrup formed on the surface. The syrup was soluble in alcohol, insoluble in ether and chloroform, and very soluble in water. It was dissolved in water, and the solution evaporated to dryness in a vacuum (Found: N, by Kjeldahl's method, 14·2; P, 21·5%). These figures correspond to the figures for *guanidine diethyl pyrophosphate*, which requires N, 14·2; P, 21·4%.

That the compound is a salt was shown by the formation of the yellow crystalline guanidine picrate on addition of a concentrated solution of picric acid. The precipitate was separated from picric acid by washing with ether and had the correct m. p. of 316°. It contained no trace of phosphorus (Found: N, 29·3. Calc. for $CH_5N_3,C_6H_3O_7N_3$: N, 29·1%). This compound again is a salt of ethyl dihydrogen phosphate.

Summary.

By the action of various alcohols on ethyl metaphosphate there has resulted a mixture of esters of phosphoric acid and usually a mixed ether, sometimes a simple ether. The products are more easily reviewed by reference to the following list.

Alcohol taken.	Esters formed.	Ethers.	Alcohol taken.	Esters formed.	Ethers.
Ethyl	Monoethyl		Phenol	Monophenyl	Ethyl phenyl
	Diethyl			Diphenyl	
Propyl	Monopropyl			Monoethyl	
	Dipropyl	Dipropyl		Diethyl	
	Monoethyl		Chol-esterol	Monochol-esteryl	Ethyl chol-esteryl
	Diethyl				
Cetyl	Monocetyl	Ethyl cetyl		Monoethyl	
	Dicetyl	Dicetyl			
	Monoethyl				
	Diethyl				

The use of ethyl metaphosphate for preparing esters of phosphoric acid, on account of the mixtures produced, is not recommended. It has no advantage over the reaction of alcohol and phosphoric oxide.

The reaction of ethyl metaphosphate with ammonia, hydrazine, alanine, guanidine, and other amino-compounds yields salts of ethyl metaphosphate, which are converted by water into salts of ethyl dihydrogen phosphate, or of diethyl dihydrogen pyrophosphate. It has not been possible to isolate any compound with the composition described by Langheld, or by Strecker and Heuser, in which nitrogen is directly combined with phosphorus.

ST. THOMAS'S HOSPITAL MEDICAL SCHOOL. WESTMINSTER SCHOOL.
[*Received, October 29th,* 1928.]

XLV.—*The Preparation of α- and β-Methylglucoside.*

By THOMAS STEWART PATTERSON and JOHN ROBERTSON.

BEING recently engaged on work in which α-methylglucoside was equired in some quantity, we attempted to simplify Emil Fischer's aethod of preparation (*Ber.*, 1895, **28**, 1151), and found that this ompound can be far more easily obtained merely by boiling pure lucose with methyl alcohol and hydrogen chloride under reflux, han by means of sealed tubes. We then discovered that Bouruelot (*Ann. Chim.*, 1915, **3**, 298) had already prepared α-methyllucoside by boiling glucose with methyl alcohol containing 0·25% f hydrogen chloride for 80 hours, obtaining a yield of about onenth the glucose used, and that Hudson (*J. Amer. Chem. Soc.*, 925, **47**, 266), in consequence of Bourquelot's work, had prepared ethylxyloside and some similar compounds in an analogous way

but in a much shorter time. These preparations, being incidental, are not indicated in the titles of the papers and so may easily be overlooked. At this stage we received "Organic Syntheses," Vol. VI, in which the preparation of α-methyl-*d*-glucoside is described, p. 64. According to the method there given, a total yield of 48·5—49·5% of the theoretical may be obtained by boiling glucose for, altogether, 228 hours—nearly 10 days—with methyl alcohol containing 0·25% of hydrogen chloride, but this, the most recent procedure, does not seem to us to be by any means the best, and therefore it may be of use to others if we describe the process which we have found to be the most advantageous. It has been arrived at after a considerable number of trials, in which the time of boiling and the quantity of hydrogen chloride present were varied, the operations being controlled by the polarimeter.

The quality of the glucose is an important factor in the success of the preparation. We used that supplied by the British Drug Houses as *dextrose pure anhydrous.* Of this material, 200 g. were dissolved in 400 g. (half the quantity recommended by Fischer) of methyl alcohol, carefully dried over lime and containing 3% of hydrogen chloride. The rotation of the resulting mixture, determined as soon as possible after the glucose had gone into solution, was $\alpha_{5461}^{17°}$ (100 mm.) = *ca.* + 10°. The solution was then boiled on the water-bath under reflux for 4½ hours, 5 g. of good animal charcoal having been added 10 minutes before the end of this time. The rotation had then risen to *ca.* + 36° and longer boiling produced little further change. In another experiment, after 24 hours' boiling, the rotation was + 41·5°.

(A) The solution was then filtered rapidly and cooled in ice-water with occasional stirring. In the course of ¾ hour the reaction mixture formed a thick paste. The α-methylglucoside was filtered off and, after being washed with a little methyl alcohol, dried on porous plate. The yield was 82 g. of m. p. *ca.* 163°.

(B) From the mother-liquor some 200 c.c. were distilled off. The residue, after treatment with charcoal as before and cooling in ice-water, etc., yielded another 44 g. of α-methylglucoside having m. p. 155—160°; making a total yield of 126 g. of crude product (61·5% of the theoretical after only a short period of boiling).

(C) From this crude yield, after recrystallisation from methyl alcohol (140 g. requires 350 c.c. of alcohol) and working up of the mother-liquors, 92 g. of pure α-methylglucoside were obtained of m. p. 165—166° and rotation $[\alpha]_D^{12·0°}$ (*c* = 1·0443 in water) = +157·9°.

(D) The mother-liquor from (B), cooled in a freezing mixture and seeded with β-methylglucoside, yielded, on standing over-night, 16 g. of crude β-methylglucoside of m. p. 98—100°.

(E) The mother-liquor from (C), on standing, gave, without seeding, 3 g. of crude β-methylglucoside of m. p. 104—105°.

The crude products from (D) and (E) on recrystallisation from methyl alcohol yielded 10·2 g. of β-methylglucoside of m. p. 107—108° and rotation $[\alpha]_D^{15^\circ}$ (c = 0·303 in water) = − 26·38°. This, recrystallised from methyl alcohol, gave 4·8 g. of pure β-methylglucoside of m. p. 110° and rotation $[\alpha]_D^{15^\circ}$ (c = 0·276 in water) = − 31·97°.

It will readily be understood that there is a disproportionate loss in recrystallising an easily soluble substance like β-methylglucoside in small quantity, but it appears from our experiments that with a total time of boiling of only 4½ hours it is quite easily possible to obtain 42·6% of the theoretical yield of α-methylglucoside and at least 2·5% of the theoretical yield of β-methylglucoside or 45·1% in all. From the mother-liquors still further quantities of both the α- and the β-derivative may be obtained, but their recovery is probably not worth the time spent upon it, unless the mother-liquors from several preparations are worked up together.

If, after stage (B), the mother-liquors are boiled, with addition of more hydrogen chloride, under reflux for a further period, more α-methylglucoside is produced at the expense of β-methylglucoside, and the yield of the former can be increased. In this way, aiming at a maximum prodnction of α-methylglucoside, we succeeded, in several preparations, in raising the yield to 75% of the theoretieal, but this increased yield does not repay the trouble it involves.

Although we have described the above experiment to show what may be obtained after 4½ hours' boiling, the best practical procedure for the preparation of α-methylglucoside would be to boil over-night and work up the product next morning.

UNIVERSITY OF GLASGOW. [*Received, December 15th*, 1928.]

XLVI.—*The Electrolytic Reduction of the Imides of Cyclic Acids (Preliminary Note).*

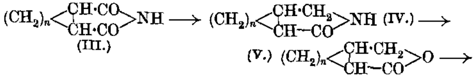
By KOTTIAZATH NARAYANA MENON and JOHN LIONEL SIMONSEN.

THE methods available for the preparation of cyclic acids of type (I) are somewhat limited in number, and as we have for some time been interested in the synthesis of homocaronic acid (II) we attempted to devise a general method for their preparation. Although our experiments are in many respects incomplete, we have decided to place them on record, since we can no longer collaborate and work

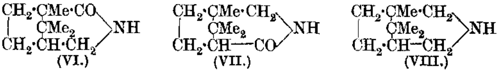
in a related field has recently appeared (*J. Indian Chem. Soc.*, 1928, **5**, 549).

(I.) (II.)

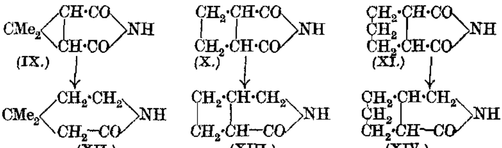
After reviewing the literature, the most promising avenue of approach seemed to us to be that indicated by the following scheme :


(III.) (IV.) (V.) (I.)

So far as we are aware the only previous description of lactams of type (IV) is that of the isomeric α- and β-camphidones (VI and VII) which were obtained by Tafel and Eckstein (*Ber.*, 1901, **34**, 3274)


(VI.) (VII.) (VIII.)

by the electrolytic reduction of camphorimide, the fully reduced base, camphidine (VIII), being also formed (compare Hope and Lankshear, P., 1913, **29**, 224). We decided, therefore, to investigate the electrolytic reduction of the imides of some typical cyclic acids and selected *caronimide* (IX), cyclo*butane*-1 : 2-*dicarboxylimide* (X),


(IX.) (X.) (XI.) (XII.) (XIII.) (XIV.)

and *cyclopentane-1 : 2-dicarboxylimide* (XI). The reduction of (X) and (XI) proceeded smoothly with formation of the expected lactams (XIII and XIV) and no evidence was obtained of the formation of the fully reduced base corresponding to (VIII); the yield of the reduction product from caronimide, however, was small (5%) and it was found that the reduction had proceeded further with fission of the *cyclo*propane ring and formation of 4 : 4-*dimethyl*-2-*piperidone* (XII), a substance which should be obtainable more directly from ββ-dimethylglutarimide. The electrolytic reduction of caronimide proceeds, therefore, in a manner analogous to the catalytic reduction of carone (Iyer and Simonsen, J., 1926, 2049) and the reduction of caronic anhydride with sodium

and alcohol (Hariharan, Menon, and Simonsen, J., 1928, 431), where also the rupture of the *cyclo*propane ring was observed. The marked instability of this ring to reducing agents is noteworthy but cannot be considered as altogether contrary to views which have been expressed previously as to the effect of substituents on the stability of rings (*inter alia*, J., 1907, **91**, 817; 1914, **105**, 2665, 2685; 1923, **123**, 113; *J. Amer. Chem. Soc.*, 1916, **38**, 1520; 1917, **39**, 1404; *J. pr. Chem.*, 1903, **68**, 156).

The two lactams, which crystallised well, resembled closely in properties the isomeric camphidones. They could not be hydrolysed with barium hydroxide, and with nitrous acid they gave liquid nitroso-derivatives which, on treatment with dilute alkali solution, evolved nitrogen and were converted into the sodium salts of the corresponding hydroxy-acids, which await investigation.

EXPERIMENTAL.

The imides were prepared by treatment of the anhydrides with dry ammonia at 180°. They were readily soluble in water and the ordinary organic solvents.

Caronimide (IX) crystallised from water in long prismatic needles, m. p. 120° (Found: N, 10·4. $C_7H_9O_2N$ requires N, 10·1%).

cyclo*Butane*-1 : 2-*dicarboxylimide* (X) separated from chloroform–light petroleum in plates, m. p. 121° (Found: N, 11·5. $C_6H_7O_2N$ requires N, 11·2%).

cyclo*Pentane*-1 : 2-*dicarboxylimide* (XI) crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 90° (Found: N, 10·2. $C_7H_9O_2N$ requires N, 10·1%).

The following procedure was adopted for the reduction of the imides. The imide (5 g.) in sulphuric acid (50% by weight; 35 c.c.) was reduced for 7 hours at 0—5° with a current of 4·2 amps. ("current concentration" 120 amps.). The ratio of the cathode surface to the cathode space of the reduction apparatus was 1 : 1. On completion of the reaction, the neutral reduction product was isolated by repeated extraction with chloroform, the acid solution, after neutralisation with barium carbonate and filtration, was distilled with the aid of a column under diminished pressure, and the distillate examined for basic products, which, as has already been mentioned, were not found.

4 : 4-*Dimethyl*-2-*piperidone* (XII), obtained (yield, 5%) by the reduction of caronimide, was a thick oil which showed no tendency to crystallise. It gave with phosphotungstic acid a white precipitate and with phosphomolybdic acid a yellow precipitate. For analysis it was purified through the phosphotungstate, since the quantity available was insufficient for distillation (Found: C, 66·1;

H, 10·3; N, 11·3. $C_7H_{13}ON$ requires C, 66·1; H, 10·2; N, 11·0%). The benzoyl derivative, prepared by the Schotten–Baumann reaction, crystallised from dilute alcohol in glistening prisms, m. p. 114°.

γ-Lactam of 2-*Aminomethyl*cyclo*butane*-1-*carboxylic Acid* (XIII).—The lactam (yield, 15%) crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 127—128°. It was precipitated from its aqueous solution by phosphotungstic and phosphomolybdic acids and gave a liquid nitroso-derivative (Found: C, 64·7; H, 8·3; N, 12·6. C_6H_9ON requires C, 64·9; H, 8·1; N, 12·6%).

γ-Lactam of 2-*Aminomethyl*cyclo*pentane*-1-*carboxylic Acid* (XIV).—This lactam was obtained in a more satisfactory yield (25%) than that of the *cyclo*butane acid. It crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 83° (Found: C, 67·1; H, 8·8; N, 11·4. $C_7H_{11}ON$ requires C, 67·2; H, 8·8; N, 11·2%). It was unaffected by treatment with barium hydroxide solution (10%) at 180° (sealed tube), but the liquid nitroso-derivative when warmed with dilute sodium hydroxide solution (10%) evolved nitrogen with formation of the sodium salt of the hydroxy-acid, the lactone of which was deposited on warming the acidified solution. The p-*nitrobenzoyl* derivative, prepared by treatment of the lactam with *p*-nitrobenzoyl chloride in pyridine solution, crystallised from dilute alcohol in glistening leaflets, m. p. 123° (Found: N, 10·5. $C_{14}H_{14}O_4N_2$ requires N, 10·4%).

INDIAN INSTITUTE OF SCIENCE,
BANGALORE. [*Received, December 28th*, 1928.]

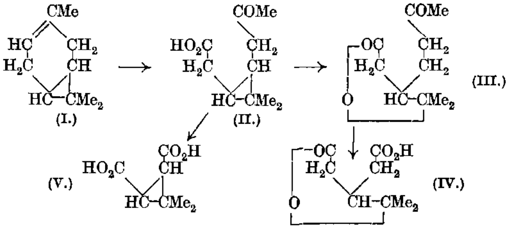
XLVII.—*Indian Turpentine from* Pinus longifolia, *Roxb. Part V. The Oxidation of* d-Δ³-*Carene with Beckmann's Chromic Acid Mixture.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

ALTHOUGH the identification of terpenes may in many cases be readily effected by the preparation of crystalline derivatives (nitrosochlorides, nitrosates, etc.), when complex mixtures are under examination these frequently fail to separate. Recently Henry and Paget (J., 1921, **119**, 1714; 1923, **123**, 1878; 1928, 70) have commenced a detailed study of the oxidation of monocyclic terpenes with Beckmann's chromic acid mixture and the results which they have obtained are of more than ordinary interest in that they would appear to afford a new and valuable method for the analysis of terpene mixtures. Before judgment, however, can be passed on the general diagnostic value of the method the investigation of

dicyclic terpenes is essential (compare Fittig and Krafft, *Annalen*, 1884, **208**, 71) and with Dr. Henry's consent we have now studied the action of this reagent on *d*-Δ^3-carene.

The oxidation of this hydrocarbon with potassium permanganate (J., 1920, **117**, 576; 1921, **119**, 550) and ozone (Semmler and von Schiller, *Ber.*, 1927, **60**, 1591) has resulted mainly in the formation of acids containing the *cyclo*propane ring, but with the Beckmann reagent, owing doubtless to its strongly acidic properties, the oxidation proceeds in two directions, *l*-*trans*-caronic acid (V) and terpenylic acid (IV) being produced in relatively large yield and *d*-homoterpenyl methyl ketone (III), terebic acid, *cis*-caronic acid, and dimethylmalonic acid in small quantities.



The isolation of *d*-homoterpenyl methyl ketone proves that the oxidation proceeds in accordance with the scheme set forth above, the primary product being the keto-acid (II), the *cis*-modification of which was prepared by Semmler and von Schiller (*loc. cit.*). By hydration and fission of the *cyclo*propane ring this would lead to homoterpenyl methyl ketone and its degradation products terpenylic and terebic acids; on the other hand, direct oxidation without fission would yield caronic acid (V). The separation, however, of *l*-*trans*-caronic acid was unexpected and the possible significance of this is discussed below. The intermediate formation of the keto-acid (II) is not without interest, since it provides corroborative evidence that the mechanism of the oxidation of the hydrocarbon with potassium permanganate suggested previously (*loc. cit.*, p. 551) is correct and eliminates definitely the possibility of the ethylenic group occupying the Δ^2-position.

In the case of α-pinene the direct oxidation products (pinonic acid, etc.) possess the *cis*-configuration and from analogy it might be expected that the same would apply in the case of Δ^3-carene. This would appear to be all the more probable since a consideration of a model of the formula of the hydrocarbon shows the *cis*-con-

figuration to be the one involving the least strain. If this be the case, the keto-acid (II) would be expected to be the *cis*-acid and should lead on further oxidation to *cis*-caronic acid. Our experiments have, however, shown that *cis*-caronic acid is formed only in minimal quantity, whilst *l*-*trans*-caronic acid is obtained in a large yield. *This can only be accounted for in one of two ways : (i)* that the hydrocarbon and the keto-acid derived therefrom have the *trans*-configuration or (ii) that, although the *cis*-keto-acid is first formed, the configuration of the acid is the less stable one and that either prior to or during the oxidation it passes into the more stable *trans*-form. The rearrangement, if such it be, must take place before oxidation to the caronic acid stage, since the acid obtained is optically active. We incline to the view that the hydrocarbon has the *cis*-configuration and that the *trans*-caronic acid results from either the *cis*-keto-acid or *cis*-homocaronic acid, the *trans*-configuration of either the one or the other of these acids being the more stable form under the conditions of the experiment. We do not consider that we should be justified in arguing that the formation of *l*-*trans*-caronic acid implied a *trans*-configuration for the terpene, an assumption which would only be justified, as Professor Lapworth (private communication) has pointed out, if we could definitely prove that the *cis*-configurations of all the possible intermediate products were under the conditions of the experiment the most stable configurations.

Although *trans*-caronic acid can now be prepared with comparative ease, so far as we are aware it has not been resolved, and therefore we have no criteria as to the optical purity of the acid obtained. It is clearly a mixture of the *l*-acid with the *dl*-acid, since the observed rotatory power is much lower than that of a specimen obtained by Staudinger and Ruzicka (*Helv. Chim. Acta*, 1924, 7, 206) by the oxidation of chrysanthemum dicarboxylic acid. These authors found that the m. p. (210°) of the *lævo*-acid was almost identical with that of the racemic acid (213°): our acid has m. p. 202°. An attempt to increase the optical purity by crystallisation of the strychnine salt was unsuccessful. The diastereoisomeric strychnine salts have apparently almost equal solubilities and possibly the strychnine salt of the *dl*-*trans*-caronic acid is a partial racemate. It would be interesting to carry out the resolution of *dl*-*trans*-caronic acid with a view to the construction of the equilibrium diagram of the *d*- and *l*-isomerides.

These experiments show that the method of Henry and Paget may be used as an aid in the analysis of mixtures of dicyclic terpenes. The formation of homoterpenyl methyl ketone and terpenylic acid would be of no diagnostic value, since they can originate equally

well from pinene, but the production of caronic acid would definitely prove the presence of Δ^3-carene. At present it is impossible to say whether Δ^4-carene would behave similarly, but it is hoped to examine the oxidation of this rare hydrocarbon under similar conditions.

In view of the somewhat ready fission of the *cyclo*propane ring during the course of these experiments it seemed desirable to study once more the action of sulphuric acid on Δ^3-carene. It was important to investigate this, since, if either limonene or terpineol resulted, the formation of some of the oxidation products would be readily explained. Previous experiments (*loc. cit.*, p. 574) had shown that Δ^3-carene was not attacked by aqueous sulpburic acid (5%) at 100° and we therefore examined the action of this acid in acetic acid solution. Under tbe conditions given on p. 310 the main product formed was a *diterpene* together with a small amount of a mixture of monocyclic terpenes and a trace of *l*-borneol. The last probably owes its formation to the presence of a little pinene or camphene in the Δ^3-carene used. The diterpene did not yield any crystalline derivatives and therefore its constitution and its relationship to other known diterpenes remain undetermined. The monocyclic terpene also remained unidentified, since it did not yield any crystalline derivatives.*

EXPERIMENTAL.

A mixture of the Beckmann reagent (1500 c.c.) and *d*-Δ^3-carene (75 c.c.) was shaken mechanically for 6 days, the bottles being periodically opened to release the pressure due to the generation of carbon dioxide. The unattacked hydrocarbon (identified as Δ^3-carene) was separated, and the aqueous solution extracted with ether in a constant-extraction apparatus. The ethereal extract was washed with sodium carbonate solution (A) to remove the acidic products of the oxidation, dried over sodium sulphate, and evaporated. The small quantity of a viscid oil that remained was distilled under diminished pressure (18 mm.), the main fraction passing over at 200—210° (yield, 3 g. from 220 c.c. of the terpene). The oil was mixed with an excess of semicarbazide acetate and the *semicarbazone*, which separated immediately, was collected, washed with ether to remove adhering oil, and recrystallised from water con-

* We desire to take this opportunity of correcting a mis-statement in a paper by Mulany and Watson (*J. Ind. Chem. Soc.*, 1926, **3**, 258) that Indian turpentine contains very little pinene. The total distillate from the oleoresin from *P. longifolia* contains approximately 30% of *a*- and *β*-pinenes, an observation amply confirmed by the very careful experiments of Dupont (*Ann. Chim.*, 1924, **1**, 244), who found that the oil contained 2·8% of *a*-pinene and 9·7% of *β*-pinene. Mulany and Watson would appear to have worked with an abnormal oil.

taining a little alcohol; it then separated in aggregates of irregular prisms, decomp. 195—196° (Found: C, 54·9; H, 7·9. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9%). The rotatory power was determined in alcoholic solution at 20°: $c = 0{\cdot}1998$, $l = 4$, $\alpha_{5461} = +0{\cdot}40°$, whence $[\alpha]_{5461} = +49{\cdot}9°$.

The semicarbazone, which was insoluble in sodium carbonate solution, was hydrolysed by warming with dilute sulphuric acid (5%), and the *d*-homoterpenyl methyl ketone thus formed extracted with ether. After removal of the solvent the residual oil rapidly solidified and then crystallised from water in radiating needles, m. p. 42—43° (Found: C, 64·9; H, 8·7. Calc.: C, 65·2; H, 8·7%). The rotatory power was observed in aqueous solution at 20°: $c = 0{\cdot}4902$, $l = 4$, $\alpha_{5461} = +1{\cdot}09°$, whence $[\alpha]_{5461} = +55{\cdot}7°$. The identity of this ketone with *d*-homoterpenyl methyl ketone was confirmed by its oxidation to terpenylic acid by Wallach's method (*Annalen*, 1893, **277**, 118). The acid, after crystallisation from water, melted at 57°, and at 88—89° after drying over sulphuric acid.

The sodium carbonate solution (A) was concentrated in a current of carbon dioxide, extracted twice with ether to remove any neutral oil, acidified, and repeatedly extracted with ether. The dried ethereal extract on evaporation yielded an oil which partly crystallised. The solid acid (10 g.) was collected, washed with ether to remove liquid acids (B), and purified by crystallisation from hot water, from which it separated in glistening prisms which melted not quite sharply at 201—202°. This m. p. was not altered by recrystallisation from water or by purification through the ammonium salt. The identity with *l-trans*-caronic acid was proved by analysis (Found: C, 52·9; H, 6·4; *M*, 159·1. Calc.: C, 53·2; H, 6·3%; *M*, 158) and by its conversion into *cis*-caronic acid, m. p. 174°, which was unchanged on admixture with an authentic specimen. The rotatory power was determined in alcoholic solution at 20°: $c = 1{\cdot}9054$, $l = 4$, $\alpha_{5461} = -0{\cdot}94°$, whence $[\alpha]_{5461} = -12{\cdot}3°$. For reasons which have already been given, a portion of the acid was converted into the strychnine salt, which crystallised from water, in which it was somewhat readily soluble, in long needles. The m. p. and the rotatory power of the acid regenerated from the crystalline strychnine salt and from the strychnine salt remaining in the mother-liquor were identical with each other and with the above ($[\alpha]_{5461}$ − 11·4° and − 12·46° respectively).

The liquid acids (B) (30 g.), from which the *l-trans*-caronic acid had been separated, were heated with an equal volume of acetyl chloride on the water-bath for some hours. The excess of acid chloride was removed and after the addition of ether the well-cooled solution was washed with dilute sodium carbonate solution (C)

and dried and the ether evaporated. The residual oil (7 g.) was esterified with alcohol and sulphuric acid, and the ester distilled under diminished pressure (10 mm.); the main fraction (3 g.) passed over at 140—160°. This was hydrolysed with methyl-alcoholic potassium hydroxide solution and, after removal of the alcohol, the acidified solution was extracted with ether. Removal of the solvent left a thick oil which partly crystallised. After draining on porous porcelain, the solid acid was recrystallised from water and was identified as *cis*-caronic acid, m. p. 174°, both alone and after admixture with an authentic specimen. The higher- and lower-boiling fractions of the ester gave on hydrolysis oils which showed no tendency to crystallise and were not further examined.

The sodium carbonate solution (C), after concentration in a current of carbon dioxide, was acidified and extracted with ether. The liquid acid obtained was esterified, and the ester repeatedly fractionated under diminished pressure (16 mm.); ultimately three fractions were obtained, (i) below 140°, (ii) 140—155°, and (iii) 155—173°. Fraction (i) (3 g.) on hydrolysis with methyl-alcoholic potassium hydroxide solution gave a liquid acid smelling strongly of a lower fatty acid (? *iso*butyric acid) which on long keeping deposited crystals. After draining on porous porcelain and crystallising from a little water, the acid was found to decompose at 185°, and further crystallisation from benzene raised this to 188—190°. This acid was dimethylmalonic acid (Found : M, 131·8; calc., 132).

Fraction (ii) (4 g.) gave on hydrolysis a small amount of a crystalline acid which after purification from water had m. p. 173—174° and was identified as terebic acid by the method of mixed m. p.

Fraction (iii) (15 g.) boiled at 168—173°/16 mm. on redistillation and when cooled in a freezing mixture crystallised in needles, m. p. 37—38°. This was identified as ethyl terpenylate by hydrolysis to the acid, which after crystallisation from water had m. p. 57°, the m. p. rising after dehydration over sulphuric acid to 90°. The composition was confirmed by titration with cold and hot alkali (Found : M, 187, 189·1; calc., 190).

Action of Sulphuric Acid on d-Δ^3-*Carene*.—A mixture of the hydrocarbon (100 g.), acetic acid (250 g.), and sulphuric acid (50%; 10 g.) was heated at 60° (thermostat) for 4 hours. The solution, at first homogeneous, gradually separated into two layers. After cooling, the acid was removed by the addition of sodium carbonate, the oil separated, mixed with an excess of alcoholic potassium hydroxide solution, and heated on the water-bath for 3 hours. After the addition of water, the oil was again separated, dried over potassium carbonate, and repeatedly fractionated under diminished pressure; ultimately the following fractions were obtained, (i)

below 120°/100 mm., (ii) 120—140°/100 mm., (iii) 180—185°/15 mm., (iv) above 185°/15 mm.

Fraction (iii), which was the main product of the reaction, distilled at 175°/10 mm. and its analysis corresponded to that of a *diterpene* (Found: C, 87·6; H, 11·7. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%). When freshly distilled over sodium, the diterpene is a colourless, very viscid oil with a somewhat unpleasant smell; it rapidly becomes yellow on exposure to the air. In chloroform solution, bromine is absorbed with evolution of hydrogen bromide. Dissolved in acetic acid, a drop of sulphuric acid produces a deep red coloration which slowly changes to violet and finally to a dirty brown. The following constants were observed: $d_{30^\circ}^{30^\circ}$ 0·9309, n_D^{30} 1·5168, $[\alpha]_{5461}^{20^\circ}$ + 5·69°.

Fraction (iv), which was a viscid oil with no definite boiling point, was not further examined.

Fractions (i) and (ii) were systematically fractionated at the ordinary pressure (755 mm.). The main fraction distilled at 174—176° and after distillation over sodium had $d_{20^\circ}^{20^\circ}$ 0·8500, $n_D^{20^\circ}$ 1·4750, $[\alpha]_{5461}^{20^\circ}$ − 6·5°. Treatment with bromine in either acetic acid or amyl-alcoholic solution gave an oil, and no crystalline nitrosate or nitrosite was obtained. The hydrochloride (b. p. about 115°/15 mm.) did not crystallise when cooled. In acetic anhydride solution the liquid gave no colour with sulphuric acid, showing the absence of sylvestrene. With the material available, further experiments were not possible, but neither *m*- nor *p*-cymene appeared to be present in appreciable quantity.

After removal of the terpene a small fraction, b. p. 195—205°/755 mm., was obtained which partly crystallised on keeping. The solid was collected (3 g. from 300 g. of terpene), drained on porous porcelain, and recrystallised from dilute alcohol; it then separated in glistening plates, m. p. 204—205° (sealed tube). It was identified as *l*-borneol (c = 1·218 in alcohol, l = 4, α = − 1·31°, whence $[\alpha]_{5461}^{20^\circ}$ = − 26·9°) by the preparation of the *p*-nitrobenzoyl derivative, m. p. 136—137° (compare Henderson and Heilbron, P., 1913, **29**, 381).

We wish to express our thanks to Mr. P. H. Guest, Manager of the Jallo Turpentine Factory, Punjab, for the gift of the carene used in this work. We also acknowledge our indebtedness to Messrs. Imperial Chemical Industries Ltd. and to the Government Grant Committee of the Royal Society for grants by means of which the necessary apparatus and chemicals (respectively) have been purchased.

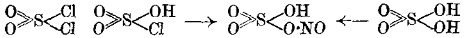
GUY'S HOSPITAL MEDICAL SCHOOL,
(UNIVERSITY OF LONDON), S.E. 1. [*Received, December 28th,* 1928.]

XLVIII.—*Nitrosylsulphuric Acid. Part II.*

By CYRIL W. HART JONES, WILLIAM JOHN PRICE, and HARRY WILLIAM WEBB.

FURTHER evidence for the presence of a hydroxyl group in nitrosylsulphuric acid (III) (compare Part I, J., 1926, 1219) has been obtained by the synthesis of the acid from chlorosulphonic acid and nitrogen tetroxide. An attempt to synthesise the corresponding dinitrosyl sulphate, $SO_2(O{\cdot}NO)_2$, from sulphuryl chloride and nitrogen tetroxide was unsuccessful. We were also unable to obtain this substance from silver nitrite and sulphuryl chloride, or by heating nitrosylsulphuric acid under pressure with nitrogen tetroxide.

A comparison of the action of nitrogen tetroxide on some of the substances we have examined is of interest. With (II) and (IV) it



(I.) (II.) (III.) (IV.)

gives (III) as the final product, whereas with (I) it does not react. These facts suggest that the type of reaction under examination occurs only when the transient formation of the substance $O_2S{=}O$ is possible, a suggestion for which there is some evidence in the reaction between nitrogen tetroxide and sulphuric acid. The modification in the properties of the second hydroxyl group in sulphuric acid caused by the substitution of the nitroso-group for the other hydrogen atom is remarkable and appears to be parallel to the activity of chlorine in chlorosulphonic acid as compared with its inactivity in sulphuryl chloride, towards nitrogen tetroxide. The facts appear to be difficult of explanation on the octet theory if the sulphur-oxygen double bonds are assumed to be semipolar, but further experimental work is in progress to elucidate this point.

Nitrosylsulphuric Anhydride.—Some confusion appears to exist concerning the structure and methods of preparation of this anhydride. From sulphur dioxide and nitrogen tetroxide, Provostaye (*Ann. Chim. Phys.*, 1840, **73**, 362) obtained a substance of empirical formula $S_2N_2O_9$, which he regarded as the anhydride, and Rose (*Pogg. Ann.*, 1839, **47**, 605) and Brüning (*Ann. Chem. Pharm.*, 1856, **98**, 377) prepared a substance of similar properties from nitric oxide and sulphur trioxide to which they gave the formula $2SO_3,N_2O_3$. On the other hand, Berl (*Z. angew. Chem.*, 1910, **23**, 2250) repeated this work and obtained a product $4SO_3,N_2O_3$, but from nitrogen pentoxide and sulphur dioxide he prepared a substance

with the properties of the anhydride to which he ascribed the constitution $S_2O_5(O{\cdot}NO)_2$. Also Manchot (*Ber.*, 1926, **59**, 2672) further examined Rose and Brüning's method and gave to his product the formula $2SO_3,NO$.

We have attempted to prepare the anhydride by the following methods: (*a*) from liquid sulphur dioxide and nitrogen tetroxide, (*b*) from sulphur trioxide and nitric oxide, (*c*) by distillation of nitrosylsulphuric acid with phosphoric oxide, (*d*) from nitrogen tetroxide and pyrosulphuric acid, (*e*) from nitrogen tetroxide and pyrosulphuryl chloride.

From (*a*) we isolated a product of empirical formula $S_2N_2O_9$, which was completely decomposed by water into sulphuric and nitrous acids and was soluble in concentrated sulphuric acid without decomposition. On distillation, a hard crystalline *substance* of *indefinite melting point was obtained with similar chemical properties* but of empirical formula $5SO_3,2N_2O_3$. Methods (*b*) and (*c*) both yielded the same product directly, whereas methods (*d*) and (*e*) yielded the same initial product as in (*a*).

Methods (*d*) and (*e*) afford evidence that the anhydride has the structure $O{\cdot}NO{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO$, which is in agreement with the properties of the substance. We have hitherto obtained no experimental evidence which supports the alternative structure for nitrosylsulphuric acid suggested in Part I (*loc. cit.*). The anhydride is unstable to heat, being partly decomposed on distillation into sulphur trioxide and nitric oxide. The *compound* $5SO_3,2N_2O_3$ is formed by the combination of sulphur trioxide with the anhydride and should be represented by the formula $2\{2SO_3{\cdot}N_2O_3\},SO_3$, there being one molecule of sulphur trioxide to two of the anhydride. In our experiments this substance was produced directly at the ordinary temperature when excess of sulphur trioxide was present (Method *b*); it is remarkably stable, having no resemblance to the theoretically analogous pyrosulphuric acid. Its chemical properties are similar to those of the anhydride; it is completely decomposed by water into sulphuric and nitrous acids and is soluble in concentrated sulphuric acid.

The reaction between sulphur dioxide and nitrogen tetroxide under pressure at laboratory temperature is represented by the equations

$$SO_2 + N_2O_4 = SO_3 + N_2O_3;\ \ 2SO_3 + N_2O_3 = 2SO_3,N_2O_3,$$

the sole products of the reaction being the anhydride and the green liquid trioxide.

The reaction between sulphur trioxide and nitric oxide has a negative temperature coefficient, for the yield of anhydride at 100° is very small, whereas at 10° it is readily formed with evolution of an

equivalent quantity of sulphur dioxide : $SO_3 + 2NO \rightleftharpoons SO_2 + N_2O_3$, the anhydride then being formed as before.

The reaction between pyrosulphuric acid and nitrogen tetroxide is analogous to that of sulphuric acid. In the case of pyrosulphuryl chloride we obtained no evidence of the formation of nitroxyl chloride (NO_2Cl), which might theoretically be expected, nitrosyl chloride being produced.

It is suggested that the ready absorption of sulphur trioxide by the anhydride affords an explanation of the discrepancies in the composition of the anhydride previously found by different workers.

EXPERIMENTAL.

Liquid nitrogen tetroxide was purified by the addition of a little fuming nitric acid and phosphoric oxide and subsequently distilled.

Preparation of Nitrosylsulphuric Acid.—The liquid tetroxide was slowly added in equimolecular proportion to chlorosulphonic acid in a moisture-free atmosphere. Nitrosyl chloride was vigorously evolved, and the residual crystalline substance was collected on asbestos and dried in a vacuum (Found : N, 10·73 ; S, 25·31. Calc. : N, 11·02 ; S, 25·10%). The methods of analysis of this and subsequent products were those described in Part I (*loc. cit.*), except that the nitrous acid was determined by the modified method of Wilkins and Webb (*J. Soc. Chem. Ind.*, 1926, **45**, 304).

Nitrosylsulphuric Anhydride.—(a) *Interaction of sulphur dioxide and nitrogen tetroxide.* Equal volumes of liquid sulphur dioxide and nitrogen tetroxide were sealed in a glass tube and kept for 24 hours at 18—20° : the residue then consisted of the green liquid nitrogen trioxide and the crystalline anhydride (Found : N, 11·96, 12·07, 11·97 ; S, 26·53, 26·43, 26·62. Calc. for $S_2N_2O_9$: N, 11·87 ; S, 27·14%). On distillation, this substance gave sulphur trioxide and nitric oxide, together with a *compound* of b. p. 324—326° (Found, in separate preparations : N, 10·46, 10·45, 10·38, 10·39, 10·42 ; S, 28·75, 28·60, 28·78, 28·75, 28·80. $5SO_3,2N_2O_3$ requires N, 10·14 ; S, 28·95%).

(b) *Interaction of sulphur trioxide and nitric oxide.* The nitric oxide, prepared by dropping 50% sulphuric acid on a concentrated solution of sodium nitrite and potassium iodide, was purified successively by concentrated sulphuric acid and solid potassium hydroxide. The sulphur trioxide was prepared by warming pyrosulphuric acid. The reaction was first examined by passing the two gases at controlled rates through a long, jacketed, glass tube maintained at temperatures from 10° to 100°. The rate of reaction at the higher temperatures was negligible, and the procedure was modified by leading nitric oxide into sulphur trioxide at 10°. The

gas was rapidly absorbed with evolution of an equivalent volume of sulphur dioxide. At first the excess of sulphur trioxide was removed from the product by gentle warming in a stream of dry air, but it was found that the final product obtained was identical with that resulting from the direct distillation of the impure substance, and the latter procedure was ultimately adopted as being more convenient and giving a purer product [Found, (1) in undistilled product: N, 9·86, 10·05; S, 28·88, 28·76; (2) in distilled product: N, 9·75, 9·97; S, 28·89, 28·80. Calc. for $S_5N_4O_{21}$: N, 10·14; S, 28·95%].

(c) *Distillation of nitrosylsulphuric acid with phosphoric oxide.* Dry nitrosylsulphuric acid was heated with an excess of phosphoric oxide at 180° until oxides of nitrogen ceased to be evolved. When the temperature was raised to 324—326°, an oily product distilled which solidified to a hard, white, crystalline mass (Found: N, 10·51, 10·43, 10·36, 10·38; S, 28·51, 28·77, 28·69, 28·72%).

(d) *Nitrogen tetroxide and pyrosulphuric acid.* Crystalline pyrosulphuric acid and liquid nitrogen tetroxide were mixed in various proportions in a sealed tube and kept at 15° for 2 hours. The residue consisted of the anhydride (Found: S, 26·78, 27·41; N, 11·38, 11·70%) and a mother-liquor containing nitric acid, and on long standing, these interacted, causing partial conversion of the anhydride into nitrosylsulphuric acid.

(e) *Pyrosulphuryl chloride and nitrogen tetroxide.* Nitrogen tetroxide was added slowly with constant shaking to pyrosulphuryl chloride in a moisture-free atmosphere at the ordinary temperature. Nitrosyl chloride was rapidly evolved and crystals of nitrosylsulphuric anhydride separated (Found: S, 26·50, 26·43; N, 11·28, 11·40%). An identical product was obtained by using liquid nitrogen trioxide instead of the tetroxide.

Summary.

Nitrosylsulphuric acid has been synthesised from chlorosulphonic acid. The reactivity of nitrogen tetroxide with certain substances has been examined and has led to the suggestion of a mechanism for the formation of nitrosylsulphuric acid. The anhydride has been prepared by several methods, two of which throw light on its structure. With sulphur trioxide the anhydride yields a stable complex, $2(S_2N_2O_9),SO_3$.

TECHNICAL COLLEGE, ASTON,
BIRMINGHAM.

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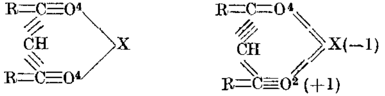
XLIX.—*The Parachor and Chemical Constitution. Part X. Singlet Linkages in Chelated Co-ordination Compounds.*

By Samuel Sugden.

In Part V of this series (J., 1927, 1173), the author suggested that the metallie derivatives of the β-diketones possessed the structure shown by the electronic formula (I).* Here both the oxygen atoms of the diketone are attached to an equivalent of the metal X by singlet linkages. According to the general theory of Sidgwick ("The Electronic Theory of Valency," Oxford Univ. Press, 1927, 52 *et seq.*), these substances would have the structure (II), in which the bond between one oxygen atom and the metal is a "co-ordinate link," *i.e.*, a duplet link in which one atom (oxygen) supplies both electrons. There is now ample stereochemical evidence for assum-

(I.)  (II.)

ing that the linkages to the metal in these substances are "directed" linkages (compare Burgess and Lowry, J., 1924, **125**, 2081; Mills and Gotts, J., 1926, 3121; Mann and Pope, *ibid.*, p. 2675), so that other formulæ involving polar bonds need not be considered.

The main object of this investigation was to ascertain whether the metallic derivatives of β-diketones exhibited the parachor anomaly which has been found in other compounds containing singlet linkages, *e.g.*, phosphorus and antimony pentachlorides (Sugden, *loc. cit.*). Compounds of uni-, bi-, and ter-valent metals with different chelate groups have been examined, and in each case the expected deficiency in the parachor has been fonnd. Before considering the experimental results it is convenient to point out one difference between the implications of the singlet and the duplet formulæ for these substances which appears to be of considerable importance.

It was first suggested by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285) that the effective charges of each atom in the molecule could be calculated by reckoning each shared electron at half its value. Numerous recent investigations on the dipole moments of molecules calculated from dielectric constants have shown that this hypothesis, whilst not strictly accurate, is substantially correct. According to Lowry's hypothesis, all organic compounds except those containing

* In these formulæ each link represents one shared electron, and the superscript numbers give the number of unshared electrons.

polar bonds (or semipolar double bonds) should have zero moment; it is found that ketones, alcohols, amines, etc., do exhibit a small moment of about 1—2 × 10^{-18} e.s.u., but this is much less than the moment corresponding to unit opposite charges on adjacent atoms separated by an atomic diameter (say 10^{-8} cm.), *viz.*, 4·8 × 10^{-18} e.s.u. Moments of this magnitude are only found with compounds, *e.g.*, nitrobenzene, which contain a semipolar double bond; hence the net atomic charges calculated on Lowry's hypothesis will probably be nearly correct. When this method is applied to formulæ (I) and (II), it is readily seen that (I) gives neutral atoms whilst (II) gives a *negative* metal atom attached to a *positive* oxygen atom. This, in the author's opinion, is highly improbable, not so much because the existence of a dipole is postulated, but because the charges ascribed to the atoms are directly opposed in sign to those which would be expected from their known electron affinity. Thus for the stable aluminium acetylacetonate, formula (II) gives an aluminium atom with three *negative* charges attached to three *positively* charged oxygen atoms; if such a structure were formed, it seems probable that the electronegative oxygen, with its high affinity for electrons, would abstract an electron from the electropositive aluminium atom, giving a rearrangement of linkages which would neutralise the atomic charges, *e.g.*, (I).

With the pentachlorides of phosphorus and antimony the polarity argument has not the same cogency. Here the duplet formula gives neutral atoms whilst the singlet formula gives a positive charge to the phosphorus or antimony, and a negative charge to two of the halogen atoms. These charges are, of course, compatible with the electrochemical character of the elements concerned.

(1) *Thallium Compounds.*

The work on thallium compounds has been greatly facilitated by the kindness of Dr. R. C. Menzies in lending specimens of thallous ethoxide, ethyl thalloacetoacetate, and dimethylthallium benzoylacetone. The parachors of these and other thallium compounds are collected in Table I and are used to determine the atomic parachor for thallium. The calculation of $\Sigma[P]$ for the co-ordinated compounds (omitting the constant for thallium) is illustrated by the case of ethyl thalloacetoacetate :

C_6 = 6 × 4·8	= 28·8	
H_9 = 9 × 17·1	= 153·9	
O_3 = 3 × 20·0	= 60·0	
2 Non-polar double bonds	= 46·4	
6-Membered ring	= 6·1	
$\Sigma[P]$ (duplets)	= 295·2.	

For the singlet formula the contribution due to two singlet linkages, 2 × (−11·6), must be included. Hence

$\Sigma[P]$ (singlets) = 272·0.

It will be seen that the full value for the six-membered ring is

TABLE I.

Substance.	Formula.	$[P]$ obs.	Singlets. $\Sigma[P]$.	Singlets. Tl.	Duplets. $\Sigma[P]$.	Duplets. Tl.
Ethyl thalloaceto-acetate	$TlC_6H_9O_3$	332·2	272·0	60·2	295·2	37·0
Dimethylthallium benzoylacetone ...	$Me_2TlC_{10}H_9O_2$	523·7	459·1	64·6	482·3	41·4
			Mean	62·4	Mean	39·2

Substance.	Formula.	$[P]$ obs.	$\Sigma[P]$.	Tl.
Thallous ethoxide ...	TlOEt	177·3	115·1	62·2
Thallous formate ...	$TlCHO_2$	150·3	80·3	70·0
Thallous acetate ...	$TlC_2H_3O_2$	183·5	119·3	64·2
Thallous nitrate ...	$TlNO_3$	177·3	92·5	(84·8)
		Mean (excluding nitrate)		65·5

included in both cases, although in the singlet formula this ring contains two singlet linkages. This treatment gives satisfactory results with all the cyclic co-ordinated compounds discussed in the present paper, even when the ring contains a larger number of singlets. Another point which should be mentioned is that no correction is introduced for the variation in size of the shell of electrons around the metallic atom. It will appear later (p. 323) that the size of this shell has no effect upon the parachor.

The two co-ordinated thallium compounds give Tl = 62·4 for the singlet formula, and Tl = 39·2 for the duplet formula. The simpler compounds of known structure in the lower part of the table show clearly that the first of these figures is correct and that the lower value given by the duplet formula is inadmissible. Thallous nitrate gives an abnormally high value for which no explanation can be offered at present. A similar large positive anomaly has been found with other salts of strong acids and bases and with certain fused metals, and will be discussed in a later paper. From all the thallium compounds except the nitrate the mean parachor is Tl = 64.

Further evidence in favour of this value is furnished by the constants for the adjacent elements in the periodic table, *viz.*, mercury and lead. For metallic mercury $[P]$ = 69·4; for mercury diphenyl $[P]$ obs. = 448·7, $\Sigma[P]$ = 380·0, whence Hg = 68·7. A carefully purified specimen of lead tetraethyl, for which the author is indebted to Dr. E. W. J. Mardles, gave $[P]$ obs. = 456·6, $\Sigma[P]$ = 380·4, whence Pb = 76·2. The sequence Hg = 69, Tl = 64, Pb = 76 is reasonable, but the value Tl = 39 is inconsistent. It is evident that the co-ordinated thallium compounds exhibit the parachor anomalies predicted for the singlet linkages in formula (I).

(2) *Beryllium Compounds.*

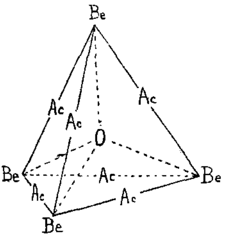
The parachors of three beryllium compounds are given in Table II; these substances were all prepared from a highly purified specimen of the oxide for which the author is indebted to Prof. J. F. Spencer.

TABLE II.

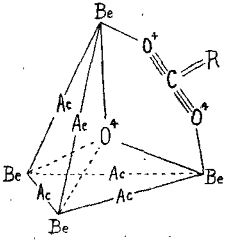
Substance.	Formula.	[P] obs.	Singlets. Σ[P].	Singlets. Be.	Duplets. Σ[P].	Duplets. Be.
Beryllium acetylacetonate	$Be(C_5H_7O_2)_2$	470·4	420·0	44·4	472·4	− 2·0
Beryllium propionylacetonate	$Be(C_6H_9O_2)_2$	539·0	504·0	35·0	550·4	−11·4
Basic beryllium propionate	$Be_4O(C_3H_5O_2)_6$	985·4	849·6	34·0	1035·2	−12·4
			Mean	37·8	Mean	− 8·6

For this element there are no suitable fusible compounds of known constitution which can be used to determine the atomic parachor independently, but a limit can be set by assuming that it must lie between the constants for the adjacent elements, lithium and boron. The data of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) for fused lithium salts give rather variable results but indicate that Li = *ca.* 50, whilst the constant for boron is 16·4 (Etridge and Sugden, J., 1928, 989). The value Be = 37·8 given by the singlet formula is compatible with these results, whereas the negative value given by the duplet formula is quite inadmissible.

The third compound in the table is one member of a series of beryllium compounds of a peculiar type. The disposition of the atoms in the molecule of the corresponding acetate has been established by *X*-ray analysis of the crystals (Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437; Morgan and Astbury, *ibid.*, 1926, *A*, **112**, 441). A unique oxygen atom occupies the centre of a tetrahedron at the corners of which the beryllium atoms are situated, and the six acyl groups span the six edges of the tetrahedron (III).



(III.)



(IV.)

This formula is readily interpreted in terms of singlet linkages as shown in (IV); it consists of six interlocked six-membered rings of which only one is shown in detail in the formula. Here, as in the

singlet formulæ for the acetylacetonates, etc., all the atoms in the molecule are neutral, and the acyl groups are disposed in such a manner as to give the symmetrical arrangement of the oxygen atoms required by the *X*-ray evidence. If the singlet linkages are replaced by duplets, unlikely polarities are produced : the beryllium atoms become negative and the central oxygen atom is assigned a charge of + 2, which is highly improbable.

An attempt was made to determine the parachor of the acetate, but its high vapour pressure at its melting point causes such rapid evaporation that trustworthy surface tension data have not yet been obtained. The next homologue has a much lower melting point and could be more easily handled; its parachor quoted in Table II is in good agreement with formula (IV), but is incompatible with the similar formula in which the singlet linkages are replaced by duplets. In computing [*P*] calc. for this substance the constant for the ring system is taken as that of 6 six-membered rings.

(3) *Aluminium Compounds.*

Table III shows the parachors of three aluminium compounds, of which the first two contain three β-diketone residues so that the difference between the values of Σ[*P*] calculated for the singlet and duplet formulæ is large. Here again the singlet formula gives a reasonable atomic parachor, Al = 38·6, whereas the duplet formula gives a negative constant. The value given by the singlet formula lies satisfactorily between the constants for sodium (*ca.* 80, from Jaeger's data on fused salts) and silicon (*ca.* 25); it is also between the constants for boron (16·4) and gallium (50·0), the last value being calculated from the observations of Richards and Boyer (*J. Amer. Chem. Soc.*, 1921, **43**, 274) on molten gallium.

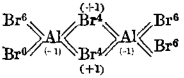
The third substance in Table III, aluminium bromide, presents some features of special interest. Its molecular weight as vapour, and in most solvents, corresponds to Al_2Br_6, and the fused substance has practically no electrical conductivity for 100° above its melting point. The polar formula $Al^{\cdots}[AlBr_6]'''$ is therefore excluded and the substance must be regarded as a covalent compound. The simplest symmetrical formula which can be written for the double

TABLE III.

Substance.	Formula.	[*P*] obs.	Singlets. Σ[*P*].	Singlets. Al.	Duplets. Σ[*P*].	Duplets. Al.
Aluminium acetylacetonate	$Al(C_5H_7O_2)_3$	680·5	639·0	41·5	708·6	−28·1
Aluminium propionylacetonate	$Al(C_6H_9O_2)_3$	788·0	756·0	32·0	825·6	−37·6
Aluminium bromide ...	Al_2Br_6	457·0	373·2	42·2	419·6	+19·0
			Mean	38·6		

molecule is shown with singlet linkages in (V) and with duplet linkages in (VI). It will be seen from Table III that (V) gives a parachor for aluminium which agrees with that found from the β-diketone derivatives, whereas (VI) gives a result which differs from the parachor given by these substances with either singlet or duplet formulæ. Moreover, (VI) is open to objection on the grounds

(V.)



(VI.)

of polarity, for it postulates negative aluminium atoms and positive bridging bromine atoms.

(4) *Unco-ordinated Derivatives of* β-*Diketones.*

In the course of this work several substances have been found which behave as if they possess an open-chain structure and do not contain the characteristic chelate ring : their parachors are collected in Table IV, which includes the free diketones as well as certain derivatives. It has frequently been assumed that a hydrogen atom

TABLE IV.

Substance.	Formula.	[P] obs.	[P] calc. (open chain).	[P] calc. (co-ordinated; singlets).
Acetylacetone	$C_5H_8O_2$	245·4	247·2	230·1
Propionylacetone ...	$C_6H_{10}O_2$	279·7	286·2	269·1
Benzoylacetone	$C_{10}H_{10}O_2$	382·4	381·1	364·0
Boron acetylacetone difluoride	$(C_5H_7O_2)BF_2$	300·6	297·5	280·4
Stannic bisacetyl-acetone dichloride	$(C_5H_7O_2)_2SnCl_2$	617·2	627·5*	591·3*

* *Sn = 56·5. This value is based on the parachors of stannic chloride and bromide, the determination of which will be described in a later communication.*

can be linked to two other atoms, as in the anion of dimeric hydrofluoric acid, F·H·F′, and can complete a chelate ring, thus giving a cyclic structure to the enol form of the free β-diketones. On theoretical grounds this structure is possible if the two links are singlets, but the hypothesis of two duplet links proceeding from a hydrogen atom appears to be incompatible with Pauli's exclusion principle (*Z. Physik*, 1925, **31**, 765), which plays such an important part in modern theories of spectra and atomic structure. The number of electrons which can occupy the *K*-level in any atom is limited strictly by Pauli's rule to two, and in the modern wave-mechanics theory of covalent linkages this restriction holds for shared electrons

also (compare Heitler and London, *ibid.*, 1927, **44**, 455; London, *ibid.*, 1928, **46**, 455). Hence the singlet structure —H— is possible, but not the duplet structure =H=.

The experimental results show, however, that the free β-diketones have but little tendency to form the chelate ring. Propionylacetone gives a parachor a little smaller than the value calculated for the open-chain formula, and this may be due to the presence of some 30% (±10%) of the cyclic isomeride. In making this estimate, the influence of the change from the keto to the enol (or dienol) structure, which might cause a small decrement due to the pressure of a free hydroxyl group, has been ignored for the following reasons. (1) The decrement is only 4—5 units in the lower alcohols and diminishes rapidly as the homologous series is ascended, so it would not be expected appreciably to affect the parachor in question. (2) By his bromine titration method, K. H. Meyer (*Ber.*, 1912, **45**, 2843) finds that pure acetylacetone is 76% and benzoylacetone 98% monoenolic; their parachors agree well with the values calculated for the diketone formula (Table IV), so the effect of enolisation is negligibly small.

The parachors found for the last two substances in the table are unexpected, but show quite definitely that these compounds are mainly open-chain derivatives of acetylacetone, *e.g.*,

$$CH_3{\cdot}CO{\cdot}CH{:}C(OBF_2){\cdot}CH_3.$$

This boron compound, examined by Morgan and Tunstall (J., 1924, **125**, 1965), differs markedly in its properties from the well-known bisacetylacetone boronium chloride. The fluoride is definitely a covalent compound, whilst the chloride gives rise to a series of salts in which the ionised chlorine atom is replaced by a number of other anions. In the tin series (Morgan and Drew, *ibid.*, p. 375) the bromide possesses properties somewhat different from those of the chloride and may have a different structure.

It is clear from the data in Table IV that a derivative of a β-diketone or any similar compound which contains chelate groups is not necessarily co-ordinated, and that the formation of the characteristic chelate ring can be detected by means of the parachor. An interesting field of investigation presents itself in the study of the conditions which favour or inhibit the formation of the ring; from the few results at present available it is clear that the nature of the metallic atom, the other groups attached to this atom, and the substituents attached to the β-diketone molecule may all play a part. In particular, the somewhat large variation in the atomic constants for beryllium and aluminium (see Tables II and III) may be due to incomplete co-ordination of the acetylacetonates at their melting point, whilst the other derivatives with lower melting points

are more completely co-ordinated. To settle this point, an investigation of the parachors of a number of beryllium compounds with different types of chelate groups is now in progress.

Discussion.

It is evident from the results described in sections (1), (2), and (3) that the parachor anomaly detected in the higher halides is reproduced in the co-ordinated compounds of uni-, bi-, and ter-valent metals, and that the parachors of all these compounds are accounted for simply and consistently by the hypothesis of singlet linkages. The higher valencies in these compounds must therefore be due to the operation of some common mechanism, and any alternative explanation in which duplet links are retained must also be capable of predicting the parachor anomaly in both series of compounds.

A little consideration of the formulæ will show that such an explanation cannot be found in the size of the electronic shell about the central atom. Thus, on the assumption of duplet linkages, the thallium atom in the co-ordination compounds studied has a shell of 6 or 8, the beryllium atom 8, the aluminium atom 12, and, in the pentachlorides, the phosphorus and antimony atoms have a shell of 10. There is no simple relation between these numbers and the observed parachor anomalies.

It is possible, however, to formulate an alternative explanation in which the duplet linkages are retained and most of the parachor anomalies accounted for. This consists in the simple hypothesis that the sharing of an electron brings about a contraction of about 12 units in the parachor.

It is convenient here to distinguish between the normal and the higher valencies of an element. The former may be defined in the following manner. If an element possesses n valency electrons, then its normal valency is n or $8-n$, whichever is the smaller. The value of this definition lies in the fact that for all substances in which the elements exert their normal valencies the chemical formulæ can be translated into electronic formulæ by replacing each chemical bond by a shared pair of electrons. Higher valencies may then be ascribed to (*a*) the transference of electrons from one atom to another as in polar bonds and semipolar double bonds, (*b*) the sharing of more than the normal number of electrons, and (*c*) the formation of singlet linkages.

The values at present adopted for the atomic parachors are in nearly every case deduced from compounds in which the constituent elements exert their normal valencies. The one assumption made in deducing these constants is that the contribution of a single chemical bond is zero. It is readily shown that this hypothesis

really means that the effect of sharing an electron is neglected. So long, however, as these constants are used to predict the parachors of other normal compounds, any error due to this omission is automatically allowed for, since each atom in the molecule is again sharing its normal number of electrons. The same compensation is found for compounds containing semipolar double bonds; thus in phosphorus oxychloride, the phosphorus atom shares 5 of its electrons with other atoms, or two more than the normal number, but this is balanced by the fact that the oxygen atom, which normally shares 2 of its 6 electrons, now shares none.

In the higher halides the singlet formula again gives the normal number shared, but the duplet formula does not Thus in phosphorus pentachloride, if all the chlorine atoms are held by duplets the total number of shared electrons is 10. In compounds in which these elements exert normal valencies the number shared is 3 for phosphorus, and 1 for each chlorine atom, giving a total of 8. In this pentachloride two extra electrons are shared, and if sharing gives a contraction of 12 units per electron, a parachor anomaly of —24 would be expected. Similarly, in the metallic derivatives of β-diketones, the formation of each of Sidgwick's "co-ordinate links" corresponds to the sharing of two extra electrons; parachor anomalies of — 24, — 48, and — 72 are therefore predicted for substances containing 1, 2, and 3 β-diketone residues, respectively. For the higher halides and the co-ordinated compounds the parachor results can therefore be accounted for by either the duplet or singlet structures.

A direct test which distinguishes between these two hypotheses is, however, provided by the data for mercury and thallium compounds (p. 318). Elementary mercury is monatomic in the vapour state and probably also as liquid; if this is the case, the mercury atom has two unshared electrons. In mercury diphenyl these electrons are shared, so that, if sharing produces a contraction, the parachor for mercury deduced from the latter compound should be smaller than that found for metallic mercury; but the experimental data give almost identical values for the mercury parachor from these two substances. A still better example is provided by the first two thallium compounds in Table I. The thallous compound possesses two unshared electrons which are shared in the dimethylthallium derivative; both substances give very nearly the same value for the parachor of thallium, thus showing that sharing an electron has little or no effect upon its contribution to the parachor.

The author has not been able to find any other simple hypothesis which will allow the duplet formulæ to be retained and will also account for the parachor anomalies. The duplet formula is in any

case open to criticism because of the improbable intramolecular polarities which it postulates. The theory of singlet, or more generally, odd-electron linkages is therefore at present the only hypothesis which gives a simple and consistent explanation of the experimental data.

One feature of the results of this investigation is the stability of valency shells of 4 electrons in the beryllium compounds and of 6 electrons in the aluminium compounds. In the light of these results it seems probable that other compounds of co-ordination number 6, *e.g.*, the cobaltammines, may also possess a stable group of 6 electrons, so that the six co-ordinated groups are held by singlet linkages. This view removes the stereochemical objections which can be raised against the arrangement suggested in an earlier paper (Sugden, *loc. cit.*, p. 1180) in which it was supposed that an octet was attained and two of the groups were held by duplets.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27) except for aluminium bromide, for which the method of capillary rise was employed (Sugden, J., 1921, **119**, 1483). Densities were in most cases determined by means of the U-shaped pyknometer described previously (J., 1924, **125**, 1171), which proved satisfactory even with substances melting above 200°. The parachor is calculated by the formula $P = M\gamma^{\frac{1}{4}}/(D - d)$, where M is the molecular weight, γ the surface tension in dynes/cm., and D and d are the densities of the liquid and the vapour. For all the substances studied, d is very small and has been neglected.

Ethyl thalloacetoacetate, $Tl(C_6H_9O_3)$, $M = 333{\cdot}1$. The specimen from Dr. R. C. Menzies melted sharply at 92° (corr.), but began to decompose above 100°. Measurements were therefore made at one temperature only: $D_{4°}^{94{\cdot}5°} = 2{\cdot}365$, γ at 94·5° = 30·94, whence $[P] = 332{\cdot}2$.

Dimethylthallium benzoylacetonate, $(CH_3)_2Tl(C_{10}H_9O_2)$, $M = 395{\cdot}2$. Dr. Menzies's specimen melted at 128—129° (corr.) and was stable up to 170°. Densities determined: $D_{4°}^{131{\cdot}5°}$ 1·797, $D_{4°}^{140°}$ 1·786, $D_{4°}^{148°}$ 1·776, $D_{4°}^{156°}$ 1·763; whence $D_{4°}^{t°} = 1{\cdot}975 - 0{\cdot}00135t$.

t	133°	142·5°	149°	157°	
γ	32·08	31·1	30·52	29·85	
D	1·795	1·783	1·773	1·763	
Parachor ...	524·0	523·4	523·7	523·8	Mean = 523·7.

Thallous ethoxide, $TlOC_2H_5$, $M = 249{\cdot}0$. Dr. Menzies supplied a pure specimen of this liquid (Found: Tl, 81·4. Calc., 81·95%).

Densities determined: $D_{4°}^{20°}$ 3·493, $D_{4°}^{38·5°}$ 3·455, $D_{4°}^{55·5°}$ 3·408; whence $D_{4°}^{t°} = 3·543 - 0·00241t$.

t	16·5°	28·5°	44·5°	
γ	38·7	37·3	36·2	
D	3·503	3·475	3·436	
Parachor	177·2	177·1	177·7	Mean = 177·3.

Thallous formate, $TlHCO_2$, $M = 249·0$, was recrystallised from methyl alcohol and melted sharply at 101° (corr.). Densities determined: $D_{4°}^{104°}$ 4·967, $D_{4°}^{115·5°}$ 4·932, $D_{4°}^{125°}$ 4·908; whence $D_{4°}^{t°} = 4·977 - 0·0028\,(t - 100)$.

t	109°	118°	124°	
γ	81·3	78·8	75·3	
D	4·952	4·927	4·912	
Parachor	151·0	150·6	149·3	Mean = 150·3.

This liquid has a high surface tension and some difficulty was experienced in getting a regular formation of bubbles. The surface tensions quoted may be slightly too high.

Thallous acetate, $TlC_2H_3O_2$, $M = 263·0$, was recrystallised from ethyl alcohol and melted sharply at 131° (corr.). Densities determined: $D_{4°}^{137°}$ 3·765, $D_{4°}^{150°}$ 3·745, $D_{4°}^{166°}$ 3·717, $D_{4°}^{181°}$ 3·691; whence $D_{4°}^{t°} = 3·999 - 0·00170t$.

t	139°	159°	173°	204°	
γ	45·4	45·0	44·9	44·5	
D	3·763	3·729	3·705	3·652	
Parachor ...	181·5	182·7	183·7	186·0	Mean = 183·5.

This substance is remarkable in showing a very small rate of fall of surface tension with temperature.

Thallous nitrate, $TlNO_3$, $M = 266·$ From the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1), $D_{4°}^{t°} = 4·923 - 0·00195t$.

t	211°	223°	231·5°	243°	
γ	112·3	111·7	110·4	109·6	
D	4·897	4·877	4·862	4·843	
Parachor ...	176·9	177·3	177·4	177·7	Mean = 177·3.

Jaeger finds rather higher surface tensions, giving $[P] = 180·7$.

Mercury, Hg, $M = 200$. The values found by different observers for the surface tension of mercury show slight variations, but these have only a small effect upon the parachor. Two modern series of measurements covering a range of temperatures up to the boiling point are those of Hogness (*J. Amer. Chem. Soc.*, 1921, **43**, 1621) and of Brown (*Phil. Mag.*, 1928, [7], **6**, 1044); the parachors calculated from these observations are given below, and since the mean values are identical, this value is adopted as the most probable.

Hogness:	t	20°	110°	200°	300°	354°	
	$[P]$	68·6	69·0	69·7	69·7	69·8	Mean = 69·4.
Brown:	t	18°	178°	218°	272°	326°	
	$[P]$	68·8	69·4	69·6	69·5	69·6	Mean = 69·4.

Both series of measurements were made with a modified form of the bubble-pressure method, which was also used by Sauerwald and Drath (*Z. anorg. Chem.*, 1926, **154**, 79), who found $\gamma_{20°} = 469$—478, whence the mean $[P] = 68{\cdot}7$, and by Bircumshaw (*Phil. Mag.*, 1928, [7], **6**, 510), who found $\gamma_{20°} = 500$, whence $[P] = 69{\cdot}8$. The measurements of Harkins and Ewing (*J. Amer. Chem. Soc.*, 1920, **42**, 2539) by the drop-weight method cover the range 0—60° and give a mean parachor of 69·0.

Mercury diphenyl, $Hg(C_6H_5)_2$, $M = 354{\cdot}1$, was recrystallised from alcohol and melted at 119° (corr.). Densities determined: $D_{4°}^{130\cdot5°}$ 1·935, $D_{4°}^{143\cdot5°}$ 1·918, $D_{4°}^{150°}$ 1·904, $D_{4°}^{166°}$ 1·882; whence $D_{4°}^{t°} = 2{\cdot}143 - 0{\cdot}00158t$.

t	129°	144°	156°	168·5°	
γ	35·97	34·63	33·42	32·75	
D	1·940	1·916	1·897	1·879	
Parachor ...	447·0	448·4	448·7	450·8	Mean = 448·7.

The author is indebted to Mr. H. J. Cavell for the observations on this substance.

Lead tetraethyl, $Pb(C_2H_5)_4$, $M = 323{\cdot}3$. Dr. E. W. J. Mardles *kindly supplied a highly purified specimen of this substance, showing* 99·7% purity. Densities determined; $D_{4°}^{18\cdot5°}$ 1·641, $D_{4°}^{28\cdot5°}$ 1·627, $D_{4°}^{40\cdot5°}$ 1·607, $D_{4°}^{48°}$ 1·595; whence $D_{4°}^{t°} = 1{\cdot}673 - 0{\cdot}00163t$.

t	20°	32·5°	45°	53·5°	
γ	28·48	27·40	26·30	25·10	
D	1·640	1·620	1·600	1·586	
Parachor ...	*455·6*	*456·5*	*458·0*	*456·1*	Mean = 456·6.

Beryllium acetylacetonate, $Be(C_5H_7O_2)_2$, $M = 207{\cdot}3$, was recrystallised from alcohol and melted at 109° (corr.). Densities determined: $D_{4°}^{111°}$ 1·017, $D_{4°}^{125°}$ 1·003, $D_{4°}^{132\cdot5°}$ 0·998, $D_{4°}^{146°}$ 0·985, $D_{4°}^{153\cdot5°}$ 0·979, $D_{4°}^{176°}$ 0·957; whence $D_{4°}^{t°} = 1{\cdot}119 - 0{\cdot}00092t$.

t	119°	120°	142°	151°	158°	169°
γ	27·6	26·6	25·3	24·6	23·8	22·9
D	1·010	1·001	0·989	0·980	0·974	0·964
Parachor	470·4	470·3	470·1	471·1	470·0	470·3
					Mean = 470·4.	

Beryllium propionylacetonate, $Be(C_6H_9O_2)_2$, $M = 235{\cdot}3$, was prepared by boiling propionylacetone (purified by recrystallisation of the copper salt) in alcoholic solution with basic beryllium carbonate, and after recrystallisation from ligroin had m. p. 52·5—53·5° (corr.). Densities determined: $D_{4°}^{64°}$ 1·035, $D_{4°}^{75°}$ 1·024, $D_{4°}^{85\cdot5°}$ 1·014, $D_{4°}^{94\cdot5°}$ 1·005; whence $D_{4°}^{t°} = 1{\cdot}096 - 0{\cdot}000964t$.

t	60°	71·5°	84°	93°	
γ	31·78	30·60	29·20	28·35	
D	1·038	1·026	1·015	1·007	
Parachor ...	**538·4**	**539·5**	**538·9**	**539·2**	**Mean = 539·0.**

Basic beryllium propionate, $Be_4O(C_3H_5O_2)_6$, $M = 490{\cdot}7$, was recrystallised from ligroin and melted at 137° (corr.). Densities determined: $D_{4°}^{142°}$ 1·056, $D_{4°}^{152°}$ 1·046, $D_{4°}^{169°}$ 1·028, $D_{4°}^{174°}$ 1·021; whence $D_{4°}^{t°} = 1{\cdot}209 - 0{\cdot}00108t$.

t	144°	150°	162°	173°	186°	
γ	20·30	19·59	18·64	17·61	16·62	
D	1·054	1·047	1·034	1·022	1·008	
Parachor	988·2	986·0	986·2	983·7	983·0	Mean = 985·4.

Aluminium acetylacetonate, $Al(C_5H_7O_2)_3$, $M = 324{\cdot}3$, was recrystallised from acetone and melted at 198° (corr.). Densities determined: $D_{4°}^{204°}$ 0·992, $D_{4°}^{215°}$ 0·978, $D_{4°}^{224°}$ 0·969, $D_{4°}^{231°}$ 0·966, $D_{4°}^{260°}$ 0·935, $D_{4°}^{279°}$ 0·914; whence $D_{4°}^{t°} = 0{\cdot}994 - 0{\cdot}00100\,(t - 200)$.

t	214°	216°	223°	232°	245·5°	278·5°
γ	18·20	17·81	17·28	16·85	15·72	13·21
D	0·980	0·979	0·971	0·962	0·949	0·915
Parachor	683·4	680·5	681·1	682·7	680·3	675·3
					Mean = 680·5.	

Aluminium propionylacetonate, $Al(C_6H_9O_2)_3$, $M = 366{\cdot}4$. This substance was obtained in good yield by shaking a concentrated aqueous solution of aluminium nitrate (1 mol.) and sodium acetate (4 mols.) with purified propionylacetone (3 mols.). The product was extracted with ligroin, and solvent and unchanged diketone were removed by heating to 100° under diminished pressure. The crude substance was a yellow oil which solidified on cooling to — 80° and then melted at 46—48°. It is very soluble in all organic solvents and was purified by dissolving in twice its volume of ligroin and cooling the solution to —15°. The crystals were filtered off on a funnel cooled by a freezing mixture, and the crystallisation was repeated. The substance was thus obtained as pale yellow crystals, m. p. 49° (corr.). Aluminium was determined by decomposing the substance in the crucible with nitric acid and igniting to oxide (Found: Al, 7·39. Calc.: Al, 7·40%). Densities determined: $D_{4°}^{53°}$ 1·087, $D_{4°}^{68°}$ 1·072, $D_{4°}^{81°}$ 1·060, $D_{4°}^{89°}$ 1·052; whence $D_{4°}^{t°} = 1{\cdot}137 - 0{\cdot}00096t$.

t	59°	65°	75°	92°	105°	
γ	29·3	28·4	27·6	25·6	24·4	
D	1·080	1·074	1·065	1·049	1·036	
Parachor	789·4	787·6	788·6	786·0	788·2	Mean = 788·0.

Aluminium bromide, Al_2Br_6, $M = 534$, purified by distillation, had m. p. 92° (corr.), b. p. 260°/754 mm. Densities determined: $D_{4°}^{104°}$ 2·628, $D_{4°}^{123°}$ 2·590, $D_{4°}^{144{\cdot}5°}$ 2·538, $D_{4°}^{161°}$ 2·497; whence $D_{4°}^{t°} = 2{\cdot}861 - 0{\cdot}00225t$. These densities are in good agreement with those of Biltz and Voigt (*Z. anorg. Chem.*, 1922, **126**, 39). Since aluminium bromide is very hygroscopic, the surface tensions were determined in a sealed tube by the method of capillary rise, the

apparatus and microscope fittings being as previously described (Sugden, J., 1921, **119**, 1483).

t	102°	120°	130°	147°	154°	
γ	25·5	24·2	23·5	22·5	21·7	
D.........	2·632	2·591	2·569	2·531	2·515	
Parachor	455·8	457·8	457·6	459·4	458·1	Mean = 457·6.

Acetylacetone, $C_5H_8O_2$, M = 100·1, purified by repeated fractionation under diminished pressure, had b. p. 60° (corr.)/20 mm. Densities determined: $D_{4°}^{11·5°}$ 0·972, $D_{4°}^{38·5°}$ 0·947, $D_{4°}^{54°}$ 0·929, $D_{4°}^{68·5°}$ 0·914; whence $D_{4°}^{t°}$ = 0·984 − 0·00101t.

t	11°	39·5°	66°	81°	
γ	32·18	28·50	25·70	24·14	
D	0·973	0·944	0·917	0·902	
Parachor	245·0	244·9	245·7	245·9	Mean = 245·4.

The author is indebted to Mr. H. Wilkins for the measurements on this substance.

Propionylacetone, $C_6H_{10}O_2$, M = 114·1, purified by recrystallising the copper derivative from benzene and distilling the regenerated diketone, had b. p. 162·5° (corr.)/759 mm. Densities determined: $D_{4°}^{15·5°}$ 0·962, $D_{4°}^{25·5°}$ 0·952, $D_{4°}^{39·5°}$ 0·939, $D_{4°}^{50°}$ 0·930; whence $D_{4°}^{t°}$ = 0·976 − 0·00093t.

t	18·5°	29·5°	41°	50°	
γ	30·38	29·24	28·10	27·22	
D	0·959	0·949	0·937	0·930	
Parachor	279·1	279·5	280·0	280·0	Mean = 279·7.

Benzoylacetone, $C_{10}H_{10}O_2$, M = 162·1, was recrystallised from ligroin and melted at 59° (corr.). Densities determined: $D_{4°}^{69°}$ 1·062, $D_{4°}^{81°}$ 1·052, $D_{4°}^{90·5°}$ 1·044; whence $D_{4°}^{t°}$ = 1·120 − 0·000804t.

t	69°	78·5°	89°	100°	
γ	39·1	38·3	37·1	35·8	
D	1·062	1·054	1·045	1·036	
Parachor	381·7	382·2	382·8	382·8	Mean = 382·4.

Boron acetylacetone difluoride, $(C_5H_7O_2)BF_2$, M = 148·0, prepared as described by Morgan and Tunstall (*loc. cit.*), melted at 46° (corr.). Densities determined: $D_{4°}^{52·5°}$ 1·220, $D_{4°}^{72°}$ 1·199, $D_{4°}^{91°}$ 1·179, $D_{4°}^{109°}$ 1·161; whence $D_{4°}^{t°}$ = 1·275 − 0·00105t.

t	60°	74°	92·5°	109°	
γ	36·18	34·55	32·89	31·29	
D	1·212	1·197	1·177	1·160	
Parachor	299·5	300·0	301·1	301·7	Mean = 300·6.

Stannic bisacetylacetone dichloride, $(C_5H_7O_2)_2SnCl_2$, M = 387·8, was prepared as described by Morgan and Drew (*loc. cit.*) and melted at 204° (corr.). Densities determined: $D_{4°}^{207°}$ 1·451, $D_{4°}^{210°}$ 1·448,

$D_{4°}^{216°}$ 1·440; whence $D_{4°}^{t°} = 1{\cdot}460 - 0{\cdot}00122(t - 200)$. This substance decomposed rapidly when heated above 225°.

t	208°	213°	221°	
γ	28·40	27·88	27·12	
D	1·450	1·444	1·434	
Parachor	617·5	617·0	617·1	Mean = 617·2.

Summary.

(1) The parachors of a number of thallium, beryllium, and aluminium derivatives of β-diketones have been determined and found to exhibit precisely the negative anomalies predicted by the author (J., 1927, 1179). Basic beryllium propionate and aluminium bromide are also found to contain singlet linkages in the molecule, and structures are suggested for these compounds.

(2) An alternative hypothesis to account for these negative anomalies has been examined and is shown to be incompatible with the available data for mercury and thallium compounds.

(3) The free β-diketones and certain derivatives are found to possess an open-chain structure and are not co-ordinated.

(4) The following atomic parachors have been determined: Hg = 69, Tl = 64, Pb = 76, Be = 38, Al = 39.

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BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, December 6th*, 1928.]

L.—*Hexa-aminobenzene.*

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

WHEN 2 : 4 : 6-trinitro-1 : 3 : 5-triaminobenzene was obtained for the first time by Jackson and Wing (*Amer. Chem. J.*, 1888, **10**, 282), these authors, as well as Palmer (*ibid.*, 1892, **14**, 378), attempted to reduce it to hexa-aminobenzene. But alcoholic ammonium sulphide led to decomposition; with tin or stannous chloride and hydrochloric acid, and with zinc dust and acetic acid, ammonia was invariably produced through the elimination of an amino-group, so that only a hydrochloride of penta-aminobenzene could be isolated. Jackson and Wing therefore concluded that hexa-aminobenzene, if actually formed, must be very unstable; and Palmer thought that "the results here noted appear to establish the fact that upon reduction of trinitrotriaminobenzene at least one nitro-group is replaced by hydrogen."

On theoretical grounds (see below) we were unable to agree with these deductions. If *salts* of hexa-aminobenzene were primarily produced, in which only some of the amino-groups would presumably be combined with the acid, then under the above experimental conditions these salts might conceivably be less stable than salts of penta-aminobenzene. But hexa-aminobenzene itself should certainly be more stable than penta-aminobenzene. If this view was correct, then it should be feasible to obtain hexa-aminobenzene, provided that every possibility of preliminary salt formation were excluded.

It has long been known that many mononitro-compounds can be reduced to amines by means of phenylhydrazine, and *m*-dinitrobenzene has been similarly reduced to *m*-phenylenediamine (Walther, *J. pr. Chem.*, 1896, **53**, 433), but polyamino-compounds do not appear to have been prepared by this method. We decided to try it, and the very first test-tube experiment, wherein trinitrotriaminobenzene was heated with phenylhydrazine, yielded *hexa-aminobenzene*. By a fortunate coincidence, phenylhydrazine is one of the very few solvents for trinitrotriaminobenzene, aud it is the *only* organic substance in which hexa-aminobenzene has, so far, been found to be soluble. Accordingly, hexa-aminobenzene can be recrystallised from phenylhydrazine. Since the synthesis trinitrobenzene ⟶ 3 : 5-dinitroaniline ⟶ pentanitroaniline ⟶ trinitrotriaminobenzene ⟶ *hexa-aminobenzene* involves only a single, simple reaction for each stage, the yields being nearly quantitative in the third stage and reasonably good in the others, hexa-aminobenzene is fairly accessible.

Penta-aminobenzene had already been known in the form of its trihydrochloride (see above; also Barr, *Ber.*, 1888, **21**, 1547; Palmer and Jackson, *Amer. Chem. J.*, 1889, **11**, 448), but the free base could not be prepared therefrom. This is not surprising, since we found that a solution of free penta-aminobenzene in water decomposes almost instantaneously. We have now accomplished the synthesis of this base by heating 2 : 4 : 6-trinitro-1 : 3-diaminobenzene with phenylhydrazine. This new base is even more accessible than hexa-aminobenzene, since there are now only three stages, starting from a commercial product: *m*-nitroaniline ⟶ tetranitroaniline ⟶ trinitrodiaminobenzene ⟶ penta-aminobenzene, each stage again consisting of a single reaction.

In accordance with our anticipations, hexa-aminobenzene has been fonnd to be distinctly more stable than penta-aminobenzene, not only in aqueous solution, but also as a solid. Both compounds share ready solubility in water and insolubility in the usual organic solvents. Both melt with decomposition, in air at temperatures

which vary with the rates of heating (varying degrees of oxidation); the true melting-decomposition points are obtained in hydrogen, 247—248° for the hexa- and 228° for the penta-aminobenzene (heating at the rate of 5° per minute). Acetic anhydride transforms hexa-aminobenzene into its *hexa-acetyl* derivative. From an aqueous solution of the free base, picric acid precipitates a *tri-picrate*, and hydrochloric acid a *tetrahydrochloride*. The latter salt is characteristic for hexa-aminobenzene, since it is formed under various conditions; a higher hydrochloride could not be obtained even with hydrochloric acid saturated with hydrogen chloride at −15°.

It is of theoretical interest to compare the phenylenediamines and all known polyamino-derivatives of benzene, of its homologues, and of anisole in their order of decreasing resistance to atmospheric oxidation. Compounds containing distinctly "negative" substituents, such as nitro- or halogeno-polyamino-derivatives, must, however, not be included, since such substituents have *per se* a stabilising effect towards oxidising agents (polar factor). In the following comparison, the relative stabilities of all the tri- and tetra-amino-compounds appear to follow from their descriptions in the literature.

Vicinal polyaminobenzenes: $1:2 > 1:2:3 > \begin{cases}1:2:3:4\\1:2:3:4:5\end{cases} < 1:2:3:4:5:6$

Diaminobenzenes: $1:2 > 1:4 > 1:3$.

Triaminobenzenes: $1:2:3 > 1:2:4$.

Tetra-aminobenzenes: $1:2:3:4 > \begin{cases}1:2:3:5\\1:2:4:5\end{cases}$.

Non-vicinal polyaminobenzenes: $1:3 > 1:3:4 > \begin{cases}1:2:3:5\\1:2:4:5\end{cases}$.

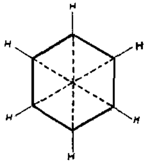
Triaminobenzenes and homologues: 1 : 2 : 3 approx. = 4-methyl-1 : 2 : 3; 1 : 3 : 4 approx. = 6-methyl-1 : 3 : 4; 2 : 6-dimethyl-1 : 3 : 5 approx. = 2 : 4 : 6-trimethyl-1 : 3 : 5.

Tetra-aminobenzenes and homologues: 1 : 2 : 3 : 4 approx. = 5-methyl-1 : 2 : 3 : 4.

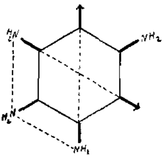
Triaminoanisoles and tetra-aminobenzenes: 1 : 2 : 3 : 4 approx. = 4-methoxy-1 : 2 : 3; 1 : 2 : 4 : 5 < 5-methoxy-1 : 2 : 4.

Clearly, (*a*) vicinal compounds are more stable than their isomerides; (*b*) vicinal as well as non-vicinal compounds become less stable as the number of amino-groups increases; (*c*) hexa-aminobenzene is the only case where, contrary to the latter rule, a further amino-group has enhanced the stability; (*d*) the introduction of methyl makes little difference; (*e*) the effect of a methoxy-group is somewhat, but not much inferior to the effect of a corresponding amino-group. It may be concluded that there is no marked purely

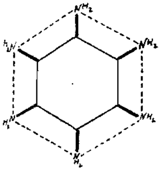
steric protection against oxidation in these cases (*d*); that groups which make a large affinity demand on the nuclear atom with which they are linked thereby alter the stable affinity distribution in the ring, destroying its aromatic character and producing centres of increased unsaturation at other nuclear carbon atoms—an effect which increases with the affinity demand of the groups ($NH_2 > O{\cdot}CH_3$) (*e*) and with their number (*b*); that this effect is diminished when the affinity demand on nuclear carbon is reduced by residual bonds (neutralisation of residual affinity) between neighbouring groups (*a*); and that substitution of an amino-group for the last remaining hydrogen atom enhances the stability of the system (notwithstanding that the residual diagonal bonds of Werner's benzene formula which characterise aromatic stability have disappeared on account of the binding of this residual affinity by the nitrogen atoms), because neutralisation of residual affinity between neighbouring nitrogen atoms (as above) is now at a maximum and also because there are now no carbon atoms of increased unsaturation, but an entirely symmetrical, although non-aromatic affinity distrihution has been achieved (*c*). These points find, to some extent, a graphical interpretation in the following formulæ, in which dashed lines denote residual bonds, and thicker lines (or thicker dashed lines) bonds (or residual bonds) with a higher affinity content; the arrows indicate enhanced free affinity.



Aromatic, stable.



Non-aromatic, uneven affinity distribution, unstable.



Non-aromatic, even affinity distribution, comparatively stable.

Experiments on the reaction of several other nitro-compounds with phenylhydrazine are dealt with in the experimental part (p. 336).

EXPERIMENTAL.

Preparation of Hexa-aminobenzene.—(a) *Attempted reduction of trinitrotriaminobenzene with stannous chloride in pyridine.* Since it seemed possible that stannous chloride might achieve the desired result in an anhydrous solvent, trinitrotriaminobenzene (1 part) and anhydrous stannous chloride (8 parts) were boiled with various

proportions of pyridine and pyridine hydrochloride in air as well as in carbon dioxide, but without success.

(b) *Reduction of trinitrotriaminobenzene with phenylhydrazine.* Numerous experiments in which trinitrotriaminobenzene was heated with phenylhydrazine in air, carbon dioxide, or hydrogen showed that the nature of the gas made little difference—presumably owing to the rapid evolution of nitrogen during the reaction. It was found, however, that with increasing proportions of phenylhydrazine the yield of crude *hexa-aminobenzene* obtained became less, but its purity was enhanced. For instance, 1·2 g. of trinitrotriaminobenzene were heated in 6 c.c. of pbenylhydrazine to 140° and kept at that temperature by external cooling until the gas evolution had ceased. Then another 5 c.c. of phenylhydrazine were added and the temperature was gradually raised to 200°. When the gas evolution had ceased, the mass was cooled: 0·380 g. of brown transparent crystals was obtained. On the other hand, when the second addition of phenylhydrazine was omitted, a 50% yield (by weigbt) of a less pure product was obtained. Similarly, 0·45 g. of the nitro-base, heated in 2·5 c.c. of phenylhydrazine in an atmosphere of carbon dioxide to 120°, kept at 120° for 40 minutes, then at 130° for 10 minutes, yielded, after cooling, dilution with benzene and filtration, as much as 0·266 g., but tbe product was black. The crude material was recrystallised from phenylhydrazine, one to three times according to its initial degree of purity, until it was obtained in small, light brown crystals, soluble in cold water without residue; the crystals were washed with benzene and brought to constant weight in a vacuum.

Properties of Hexa-aminobenzene.—It consists of small crystals—cubic octahedra, as Dr. I. E. Knaggs kindly ascertained for us—which, immediately after recrystallisation, always appear light brown in reflected light, even after seven recrystallisations. In the absence of traces of surface oxidation, it would presumably be colourless. It corresponds in this respect closely to 1 : 2 : 3-triaminobenzene (Salkowski, *Annalen*, 1872, **163**, 23), which retains the same colour, even after distillation, and appears to possess much the same stability towards atmospheric oxidation. In an atmosphere of hydrogen, hexa-aminobenzene melts with decomposition at 247—248°, after darkening from about 180° (rate of heating, 5° per minute). In air, the decomposition point, owing to oxidation, is the higher the more slowly the material is heated; at the rate of 30° per minute, the decomposition point is about 255°. Hexa-aminobenzene is moderately easily soluble in cold water and in phenylhydrazine, but insoluble in the usual organic solvents and in aniline, nitrobenzene, quinoline, benzyldiethylamine, dimethylaniline, pyridine, and amyl

alcohol. On prolonged exposure to air, the material darkens; but this is merely due to surface oxidation, since after several days it still retains its crystalline aspect and remains almost completely soluble in water, leaving behind traces of a black oxidation product. In a partly evacuated tube at $-50°$ no darkening took place in 17 hours. Dr. Knaggs found that hexa-aminobenzene appeared pale yellow in transmitted light under a microscope; the colour persisted for weeks on exposure to air, with ultimate darkening at the edges of the octahedra. The colour of the aqueous solution is light yellow, darkening to brown within a few hours; the solution deposits a black solid after about 24 hours. Even crude hexa-aminobenzene (prepared according to the first of the three examples given) is almost totally soluble in cold water, but forms a light brown and less stable solution (Found: C, 42·55; H, 7·25; N, 50·35, 50·05. $C_6H_{12}N_6$ requires C, 42·85; H, 7·15; N, 50·0%).

Hexa-acetamidobenzene.—When 1·7 parts of hexa-aminobenzene were heated in an evaporating-dish on a water-bath with 20 parts (by vol.) of acetic anhydride, a vigorous reaction ensued, and the base went into solution; then a brownish substance separated. After 5 minutes this was drained on porous plate and recrystallised from aqueous acetic acid. Yield, 1·7 parts of minute white crystals, m. p. 356—357°, decomp. p. 363° (Found: C, 51·05; H, 5·85; N, 20·2. $C_{18}H_{24}O_6N_6$ requires C, 51·45; H, 5·7; N, 20·0%).

Hexa-aminobenzene Tetrahydrochloride.—This was precipitated, whatever the concentration and temperature, when an aqueous solution of the base was run into concentrated hydrochloric acid. (1) A solution of 0·2 g. in 3 c.c. of cold water was filtered (some remained undissolved) into 10 c.c. of concentrated hydrochloric acid with good stirring and ice-cooling. Needles separated which appeared colourless in suspension, but after drying between filter-paper and then to constant weight in a vacuum had a light greyish-brown colour. Yield, 0·10 g. (Found: Cl, 45·5%). (2) 0·270 G. of the base in 5 c.c. of water was filtered into 10 c.c. of concentrated hydrochloric acid with good stirring; the filter was then washed with a further 5 c.c. of water, which was run into a further 10 c.c. of the acid. The combined precipitates weighed 0·264 g. after being dried to constant weight in a vacuum (Found: N, 27·2; Cl, 45·0. $C_6H_{12}N_6,4HCl$ requires N, 26·75; Cl, 45·2%). (3) 0·15 G. of the base in 4 c.c. of water was run, drop by drop, into 10 c.c. of concentrated hydrochloric acid saturated with hydrogen chloride at $-15°$, passage of the gas being continued during the addition of the solution of the base. The precipitate was dried to constant weight in a vacuum (Found: Cl, 45·7%).

Hexa-aminobenzene tetrahydrochloride shows no melting point,

but darkens at about 240°. It is insoluble in hot alcohol, but soluble in water. The aqueous solution turns deep brown in about 5 hours, and deposits a black solid over-night. From a saturated aqueous solution of the salt, a rapid current of ammonia gas precipitates a black amorphous powder. The solid salt, exposed to the atmosphere, does not appear to attract moisture, but becomes a black mass within 3 days. When a saturated solution of the salt is added to a 50% aqueous solution of potassium hydroxide at room temperature, a base separates in straw-coloured needles. This base yields on acetylation crystals which do not melt at 385°.

Hexa-aminobenzene Tripicrate.—One part of hexa-aminobenzene dissolved in 100 parts of water was dropped into a solution of 7 parts of picric acid in 700 parts of water at 20°. The precipitate was dried in a vacuum, ground under benzene, and dried to constant weight in a vacuum. The compound formed a dark green, infusible powder. Yield, about 2 parts (Found: C, 33·4, 33·75; H, 3·35, 2·4; N, 24·75. $C_{24}H_{21}O_{21}N_{15}$ requires C, 33·7; H, 2·5; N, 24·6%).

Penta-aminobenzene.—The following mode of preparation is typical of several reductions: 1 G. of 2 : 4 : 6-trinitro-1 : 3-diaminobenzene was heated in 10 c.c. of phenylhydrazine in hydrogen. Gas began to be evolved at 120°; at 140° the reaction became so vigorous that cooling was required. Gradually 200° was reached, at which temperature the mass was kept until the gas evolution had ceased. On cooling and filtration, 0·17 g. of dark brown crystals was obtained. Recrystallisation from phenylhydrazine in hydrogen did not alter the colour (Found: C, 47·2; H, 7·5; N, 45·4. $C_6H_{11}N_5$ requires C, 47·05; H, 7·2; N, 45·75%).

Penta-aminobenzene, in an atmosphere of hydrogen, melts with decomposition at 228° (rate of heating, 5° per minute). It is insoluble in the usual organic solvents, but soluble in water.

2 : 4 : 6-*Trinitro*-1-*amino*-3 : 5-*dianilinobenzene.*—1·0 G. of pentanitroaniline in 5 c.c. of dry acetone was slowly added, with good shaking, to 3 c.c. of aniline dissolved in 5 c.c. of acetone. The red precipitate was filtered off, washed with acetone, and dried. Yield, 1·14 g. It was obtained from nitrobenzene in minute, light red crystals, m. p. 264° (decomp.). In most other solvents this *compound* is insoluble (Found: N, 20·7. $C_{18}H_{14}O_6N_6$ requires N, 20·5%).

When the preceding compound, 2 : 4 : 6-trinitrotoluene, 1 : 3 : 5-trinitrobenzene, picramide, or 3 : 5-dinitroaniline was heated in phenylhydrazine, evolution of gas took place but nothing definite could be isolated, except in the last two cases, in which solid products, which are being examined, were obtained.

We are greatly indebted to Sir W. H. Bragg and the Royal Institution for the facilities placed at our disposal at the Davy Faraday Laboratory.

THE ROYAL INSTITUTION, W. 1. [*Received, December 7th,* 1928.]

LI.—*The Quaternary System Lead Acetate–Lead Chloride–Acetic Acid–Water at* 25°.

BY KARL SANDVED.

IN a previous paper (J., 1927, 2967) the author directed attention to the exceptional character of the ternary system lead acetate–acetic acid–water. The high solubility of lead acetate in acetic acid and the failure to isolate any acid acetates were ascribed to the existence of complex ions in the solution. Symmetrical complex ions, in which the lead atom is surrounded entirely by acetate groups, might be expected to show a high solubility in acetic acid, due to the similarity between the solute and the solvent. In the present work, lead chloride was added as a sparingly soluble fourth component in order to introduce a certain dissimilarity between solute and solvent, and hence to render more probable the precipitation of complex compounds.

According to White (*Amer. Chem. J.*, 1906, **35**, 217), various compounds are obtained by mixing solutions of lead chloride and lead acetate, for in slightly acid solutions he obtained a precipitate of composition $PbCl{\cdot}C_2H_3O_2,Pb(C_2H_3O_2)_2,\frac{1}{2}C_2H_4O_2$, and in strongly acid solutions another of formula $(PbCl{\cdot}C_2H_3O_2)_2,C_2H_4O_2$. The phase-rule investigation now described confirms the existence of these compounds and affords information on the conditions governing their stability.

EXPERIMENTAL.

The usual procedure, described in the previous paper (*loc. cit.*), was employed for separating the liquid and the solid phase. The analytical method was the same as before, with the addition of a gravimetric determination of chlorine as silver chloride.

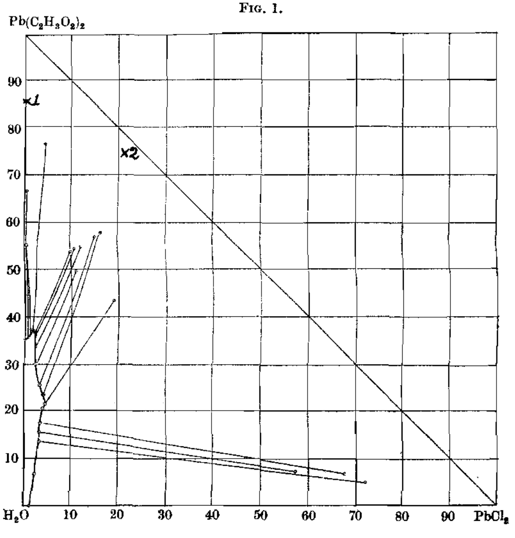
The purest quality of lead acetate from the British Drug Houses was used, and its analysis was in accord with the formula for the trihydrate. Lead chloride was precipitated from pure lead acetate solutions with distilled hydrochloric acid and twice recrystallised from hot water. Acetic acid was purified by three-fold freezing.

The System $Pb(C_2H_3O_2)_2$–$PbCl_2$–H_2O.

Precipitation of basic compounds always occurred on addition of lead chloride to neutral solutions of lead acetate. In his investig-

ation of the system $Pb(C_2H_3O_2)_2$–PbO–H_2O, Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2346) found that lead acetate trihydrate is stable as a solid up to a concentration of lead oxide equal to 15·9% ; the conditions are altered in presence of lead chloride, however, and since a study of the basic side of the diagram was beyond the scope of this work, it was found preferable to start at low concentrations of acetic acid, sufficient for dissolving the basic

FIG. 1.



compounds. This was effected in the following manner : Solutions of lead acetate and lead chloride without any acetic acid were saturated at 35°, and hydrolysis allowed to take place. After the precipitate had settled, the clear, slightly acid solutions were drawn off and cooled in a thermostat at 25°. This procedure led to complete equilibrium within 5 hours, and the crystalline solids subsided very quickly. The concentrations of free acetic acid in the solutions thus obtained were found to range between 1·4 and 1·6%. The system drawn in Fig. 1 is therefore, strictly speaking, not

ternary, but rather "pseudo-ternary," for it contains a small but practically constant amount of a fourth and independent component. From Fig. 3, in which is shown the complete quaternary system, it may be seen that Fig. 1 does not give the curves lying on the $PbCl_2$–$Pb(C_2H_3O_2)_2$–H_2O triangle of the tetrahedron, but shows the curves lying in a plane parallel to this triangle at a distance corresponding to 1·4—1·6% of acetic acid.

TABLE I.

The System Lead Acetate–Lead Chloride–Water at 25°.

No.	Liquid. PbCl₂, %.	Liquid. PbAc₂, %.	Wet solid. PbCl₂, %.	Wet solid. PbAc₂, %.	No.	Liquid. PbCl₂, %.	Liquid. PbAc₂, %.	Wet solid. PbCl₂, %.	Wet solid. PbAc₂, %.
1	1·06	—	—	—	10	2·43	30·21	11·09	49·97
2	2·07	6·91	—	—	11	2·31	33·80	12·03	54·99
3	3·01	13·47	72·00	4·95	12	2·08	36·23	10·80	54·52
4	3·30	15·71	57·19	7·29	13	2·03	36·44	9·84	53·80
5	3·68	17·88	67·50	6·75	14	1·46	37·43	4·45	76·65
6	4·00	20·63	—	—	15	1·08	36·40	0·41	55·00
7	4·48	21·25	19·01	43·50	16	0·73	35·92	0·27	66·75
8	4·13	23·70	16·29	57·50	17	—	35·53	—	—
9	3·32	25·95	15·22	56·71					

Fig. 1, constructed according to Lodočnikow's method (*Z. anorg. Chem.*, 1926, **151**, 185) from the experimental data in Table I, shows that three compounds are capable of existence at 25°, *viz.*, lead acetate trihydrate, a double compound of lead chloride and lead acetate, and finally, anhydrous lead chloride. The composition and appearance of the double compound agree with those given by White (*loc. cit.*); the silky tufts of crystals were, in fact, so characteristic that the compound was easily identified as soon as it had been precipitated. Similarly, the attainment of the invariant point between the trihydrate and the double compound was clearly marked, the large heavy needles of the former being detected without difficnlty in presence of the latter.

The two invariant points of the system lie at 1·46% $PbCl_2$, 37·43% $Pb(C_2H_3O_2)_2$, and 4·48% $PbCl_2$, 21·25% $Pb(C_2H_3O_2)_2$. The solubility of lead acetate in pure water at 25° is 35·53% and that of lead chloride 1·06%.

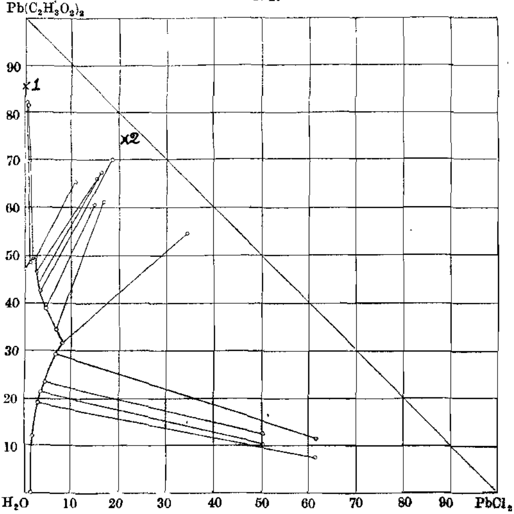
Table II and Fig. 2 represent the same system at 35°. Supersaturation was in this case effected at 42°, yielding 1·5—1·8% of acetic acid in the liquid phase. The shape of the curves is the same as in Fig. 1, and no new solid phase has appeared. The two invariant points lie at 2·17%$PbCl_2$,49·53%$Pb(C_2H_3O_2)_2$ and 7·72%$PbCl_2$,31·90%$Pb(C_2H_3O_2)_2$. The solubility of lead acetate at 35° is 47·40% and of lead chloride 1·30%.

TABLE II.

The System Lead Acetate–Lead Chloride–Water at 35°.

	Liquid.		Wet solid.			Liquid.		Wet solid.	
No.	$PbCl_2$, %.	$PbAc_2$, %.	$PbCl_2$, %.	$PbAc_2$, %.	No.	$PbCl_2$, %.	$PbAc_2$, %.	$PbCl_2$, %.	$PbAc_2$, %.
1	—	47·40	—	—	9	6·81	34·81	16·80	61·30
2	1·18	48·83	0·65	82·30	10	7·72	31·90	34·25	54·55
3	1·67	49·32	0·76	81·83	11	6·87	29·55	61·50	11·51
4	2·17	49·53	10·87	65·70	12	4·25	23·90	50·03	12·42
5	2·31	46·70	15·06	66·10	13	3·61	21·60	50·07	10·17
6	3·00	44·15	16·10	67·70	14	3·33	19·05	61·05	7·91
7	3·11	42·97	18·50	70·03	15	1·71	12·41	—	—
8	4·70	39·01	14·98	60·80	16	1·30	—	—	—

FIG. 2.

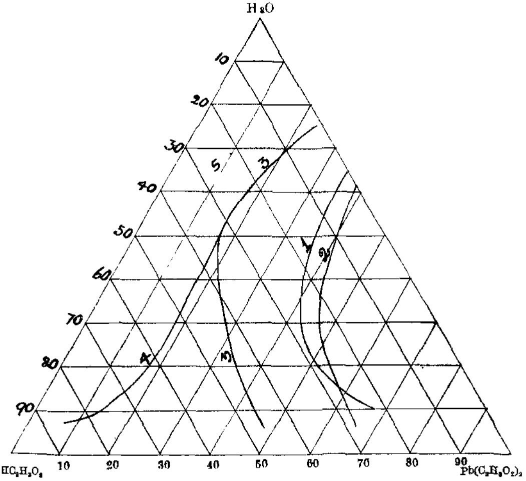


The System $PbCl_2$–$C_2H_4O_2$–H_2O *at 25°.*

Hill (*J. Amer. Chem. Soc.*, 1917, **39**, 218; see also Sandved, *loc. cit.*) and Hertz and Martin (*Z. anorg. Chem.*, 1924, **140**, 339) have

determined the solubility of lead chloride in acetic acid, but their values are all referred to unit of volume. The system has now been worked out on a weight basis, and Table III shows that pure lead chloride is the only solid capable of existence under the conditions chosen. The system is properly a quaternary system, in which lead acetate or hydrogen chloride acts as a fourth, independent component. The points obtained by determining the solubility of

Fig. 3.



lead chloride in acetic acid, therefore, merely represent points in a limited area of the system given in Fig. 3. The assumption is made that the equilibrium $PbCl_2 + 2HC_2H_3O_2 \rightleftharpoons Pb(C_2H_3O_2)_2 + 2HCl$ is displaced so largely to the left as to render negligible the concentrations of the other products. Hence the total chlorine estimated is attributed entirely to lead chloride, and the curve based on the figures in Table III is taken to represent the line of intersection between the isothermal surface 5 in Fig. 3 and the $PbCl_2$-$C_2H_4O_2$-H_2O triangle of the tetrahedron.

TABLE III.

The Solubility of Lead Chloride in Acetic Acid at 25°.

Liquid.		Wet solid.		Liquid.		Wet solid.	
$PbCl_2$, %.	HAc, %.	$PbCl_2$, %.	HAc, %.	$PbCl_2$, %.	HAc, %.	$PbCl_2$, %.	HAc, %.
1·060	—	—	—	0·481	24·83	—	—
1·024	1·28	—	—	0·372	30·32	—	—
0·983	2·33	—	—	0·273	36·99	—	—
0·883	6·01	93·01	0·87	0·213	42·20	—	—
0·793	9·58	—	—	0·147	51·72	95·21	2·41
0·723	12·71	—	—	0·084	60·40	—	—
0·627	17·27	95·15	0·81	0·047	78·30	—	—
0·547	21·31	—	—	0·013	96·60	95·61	3·20

The System $PbCl_2$–$Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O *at* 25°.

The relevant experimental data are set out in Table IV. The method of Jänecke (*Z. physikal. Chem.*, 1908, **64**, 343; 1912, **80**, 1) was found most convenient for plotting this type of quaternary system, for a rather confusing picture was obtained by Lodočnikow's method. Owing to the slight solubility of lead chloride, the various surfaces are more or less parallel to the $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O triangle of the tetrahedron, and for this reason it was found most convenient to project the entire system upon this plane as a base, as shown in Fig. 3. Only the intersection curves of the various surfaces are drawn, in order to make as clear as possible the stability conditions of each compound. The ternary system $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O, necessary for the construction of Fig. 3, has been described in a previous paper (*loc. cit.*). As pointed out there, it proved impossible to effect a satisfactory separation of the two phases at the highest concentrations of acetic acid by using the ordinary technique, and this part of the diagram has therefore not been covered.

From Fig. 3 it may be seen that four different solids, represented by four isothermal surfaces, are involved in this system, *viz.*,

Compound 1. Surface 1—2 : $Pb(C_2H_3O_2)_2,3H_2O$.
Compound 2. Surface 2—3 : $PbCl{\cdot}C_2H_3O_2,Pb(C_2H_3O_2)_2,\frac{1}{2}C_2H_4O_2$.
Compound 3. Surface 3—4 : $(PbCl{\cdot}C_2H_3O_2)_2,C_2H_4O_2$.
Compound 4. Surface 5 : $PbCl_2$.

The point representing the coexistence of 2, 3, and 4 lies at 1·44% $PbCl_2$, 17·00% $Pb(C_2H_3O_2)_2$, and 32·82% $C_2H_4O_2$.

Compound 1.—At lower concentrations of acetic acid the solubility of lead acetate increases on addition of lead chloride. Fig. 3 shows that at higher concentrations of acetic acid just the opposite takes place, the solnbility of lead acetate being diminished on addition of lead chloride.

Compound 2.—The solubility of this double compound increases

TABLE IV.

The System $Pb(C_2H_3O_2)_2$–$PbCl_2$–$C_2H_4O_2$–H_2O *at* 25°.

	Liquid.			Wet solid.		
No.	$PbCl_2$, %.	$PbAc_2$, %.	HAc, %.	$PbCl_2$, %.	$PbAc_2$, %.	HAc, %.
1	1·45	37·45	1·61	3·63	80·90	1·66
2	0·55	36·31	4·98	0·21	80·02	0·82
3	1·39	38·58	6·31	2·71	80·00	2·35
4	1·35	41·25	11·94	4·11	63·22	7·31
5	0·64	38·90	14·69	0·32	81·22	1·98
6	0·81	39·43	17·31	0·35	78·60	3·19
7	1·08	42·15	19·18	0·39	76·04	3·89
8	1·01	44·57	20·98	1·03	70·75	10·48
9	1·00	46·72	23·90	1·10	77·75	7·71
10	0·98	47·92	24·96	1·15	80·70	5·82
11	1·07	51·65	25·92	1·13	81·75	2·47
12	1·07	54·20	26·72	3·81	65·20	18·67
13	1·06	56·22	27·50	1·16	76·95	8·68
14	1·08	62·25	27·02	3·31	76·05	15·18
15	1·03	65·75	24·34	0·37	81·25	5·88
16	1·10	65·15	27·60	3·89	74·15	18·09
17	1·12	67·10	27·38	0·43	75·15	16·94
18	3·54	25·38	1·95	14·63	49·35	3·25
19	4·54	21·22	1·57	31·55	39·70	2·46
20	2·44	25·18	7·12	13·77	50·65	5·69
21	3·62	21·92	8·39	14·10	33·15	7·32
22	3·54	22·38	8·43	14·51	30·90	7·36
23	3·40	18·84	13·04	27·20	51·20	6·15
24	1·96	24·27	13·79	14·15	45·75	8·16
25	2·90	17·82	20·80	30·60	44·73	8·68
26	1·27	21·82	23·51	13·95	49·64	13·03
27	1·41	23·72	29·60	14·80	41·92	17·84
28	1·37	20·56	33·35	15·10	55·85	14·38
29	1·44	17·00	32·82	43·67	48·74	9·34
30	1·21	21·23	36·95	25·40	38·90	18·94
31	0·99	27·32	39·02	14·70	49·35	20·42
32	0·97	42·24	29·52	13·90	49·77	19·67
33	1·11	33·22	44·02	27·90	49·73	16·32
34	1·63	47·02	38·68	14·20	64·95	16·56
35	1·70	48·87	39·67	14·50	60·20	20·48
36	2·28	43·68	45·82	23·55	53·95	14·72
37	2·36	46·30	45·70	26·50	55·45	16·53
38	1·16	66·03	18·74	15·30	66·23	16·09
39	1·03	20·28	41·58	34·50	39·48	17·07
40	0·71	20·85	53·60	33·70	39·78	20·22
41	0·25	21·15	68·33	35·15	39·56	22·56
42	0·36	24·12	69·22	33·85	36·58	27·97
43	0·33	21·42	72·05	34·43	40·90	23·12
44	1·13	39·30	32·54	34·72	42·28	21·54
45	0·61	34·58	58·85	34·88	38·68	24·53
46	0·44	30·08	66·72	34·15	39·05	25·68
47	0·06	7·29	86·21	52·17	17·77	18·03
48	1·11	17·79	40·70	57·60	26·28	10·34
49	0·59	16·40	59·40	47·23	37·14	13·39
50	0·09	12·06	74·16	41·25	35·25	21·18
51	3·48	16·31	2·22	96·51	0·11	2·70
52	1·51	14·77	27·58	94·76	0·18	4·24
53	0·63	15·80	50·58	94·55	0·44	4·24
54	0·08	11·81	70·80	93·63	1·06	5·29

in just that same region where the solubility of lead acetate is subject to such a striking rise, and consequently the surface is twisted in a peculiar way, as shown in Fig. 3.

Compound 3.—This complex substance, which is sparingly soluble, is only stable over a certain range, for which the concentrations of acetic acid are high compared with those of lead acetate. At lower concentrations of acetic acid the compound becomes increasingly soluble and finally disappears as a solid through conversion into compound 2, whilst an addition of acetic acid is seen to diminish the solubility. The compound always separated as a finely divided powder, readily distinguishable from compound 2.

Compound 4.—The surface representing the solubility of lead chloride intersects the $PbCl_2$–$C_2H_4O_2$–H_2O triangle along a line corresponding to the values given in Table III. The solubility decreases on the first part of curve 3, but passes through a minimum at that point where the increase in the solubility of lead acetate occurs.

Both the type of double compound isolated and the corresponding solubility curves indicate a pronounced tendency of lead acetate to enter into reactions yielding various complex substances. The formation of the group $PbCl{\cdot}C_2H_3O_2$, involved in the two compounds, is well accounted for by the theory of Blomberg (*Chem. Weekblad*, 1914, **11**, 1030; *Z. Elektrochem.*, 1915, **21**, 438), in which the ion $Pb(C_2H_3O_2)^{\cdot}$ is supposed to play an important role (see Sandved, *loc. cit.*). This explanation is further supported by the parallelism between the solubility of lead acetate and of the double compound 2.

Summary.

The two systems $Pb(C_2H_3O_2)_2$–$PbCl_2$–H_2O and $PbCl_2$–$C_2H_4O_2$–H_2O have been studied at 25°, and the first also at 35°. Based upon these data, as well as upon the system $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O, an investigation of the quaternary system has been undertaken at 25°.

From the results, it is shown that the changes brought about by the introduction of lead chloride in these systems are in accord with the views upon lead acetate solutions advanced previously by the author.

The author's thanks are due to the Ramsay Memorial Fellowship Trust for placing a Fellowship at his disposal, and to Professor J. C. Philip, F.R.S., under whose interested direction this research was conducted.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, November 26th*, 1928.]

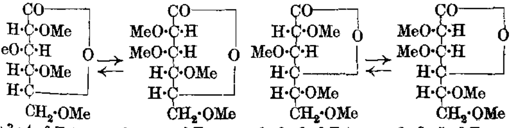
LII.—*The Conversion of Tetramethyl γ- and δ-Glucono-lactones into the Corresponding Mannonolactones, and of the Trimethyl γ- and δ-Xylonolactones into the Corresponding Lyxonolactones.*

By Walter Norman Haworth and Charles William Long.

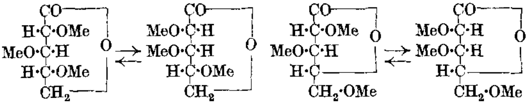
The authors have effected the epimerisation of several methylated lactones which are configurationally inter-related. Whilst the interconversion of α-hydroxy-acids is a well-recognised procedure, it has been shown that interconversion is effected just as readily when the hydroxyl groups in the hydroxy-acids are protected by methylation. Digestion with aqueous pyridine for a number of hours is sufficient to establish equilibrium between the two epimerides and the intermediate products.

One object of this investigation was to correlate a number of the methylated lactones which had already been studied in their relation to the constitution of sugars, and to supplement the evidence previously adduced of the existence of two types of ring structure. Hitherto the evidence has rested on the identification of the methoxy-dibasic acids derived from the lactones by oxidation (Haworth and Jones, J., 1927, 2349; Goodyear and Haworth, *ibid.*, p. 3136; Haworth, Hirst, and Miller, *ibid.*, p. 2436; Haworth and Porter, J., 1928, 611). The authenticity of the product depends in most cases upon a recognition of the stereochemical form of the methoxy-acid. By the inter-relationships established in the present work the evidence for the structure which has already been furnished is further strengthened. The effect is to duplicate the proofs of the ring structures of sugars and glucosides based on the original oxidation data of methylated lactones. Moreover the determination of the structure of a new methylated lactone should in future be facilitated by the adoption of this procedure, inasmuch as it may be characterised by epimerisation to a lactone of known structure.

The following interconversions have been achieved :



3 : 4 : 6-Tetramethyl δ-gluconolactone. | 2 : 3 : 4 : 6-Tetramethyl δ-mannonolactone. | 2 : 3 : 5 : 6-Tetramethyl γ-gluconolactone. | 2 : 3 : 5 : 6-Tetramethyl γ-mannonolactone.

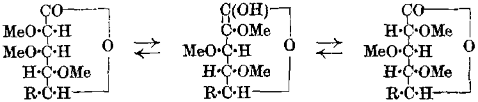


2 : 3 : 4-Trimethyl δ-xylonolactone. 2 : 3 : 4-Trimethyl δ-lyxonolactone. 2 : 3 : 5-Trimethyl γ-xylonolactone. 2 : 3 : 5-Trimethyl γ-lyxonolactone.

In each case the resulting lactone was identified by preparing from it the crystalline phenylhydrazide of the corresponding acid, and the constants of these compounds are available for future reference.

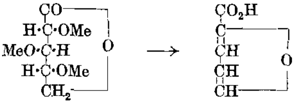
The experimental procedure differed from that adopted by E. Fischer (*Ber.*, 1890, **23**, 799) in his original work on hydroxy-acids. Whereas Fischer used quinoline or pyridine containing little water, we have used dilute aqueous pyridine, which promotes the epimerisation with extraordinary readiness even below 100°. Inasmuch as pyridine is easily eliminated from the salts by gentle heating, with the immediate formation of the methylated lactone, the removal of the organic base by means of barium hydroxide, followed by the precipitation of barium as sulphate, was obviated; as also was the use of the brucine salts for the purpose of purification, since the methylated lactones were recrystallised or distilled.

As the pyridine salts of these methoxy-acids hydrolyse readily in aqueous solution, it is evident that they are present in equilibrium with the free acids and the lactones. It has been suggested by earlier workers that epimerisation proceeds through the enolic form of the acids or salts, but it may equally be the case that the intermediate stage is represented by the enolic form of the lactones:



A comparison of the amounts of each substance occurring in the product shows that the lactone which is less easily hydrolysed by water is also the one which predominates in the epimeric mixture. Thus, in the study of the comparative rates of hydrolysis of 2 : 3 : 4 : 6-tetramethyl δ-gluconolactone and of the corresponding mannonolactone, it has already been shown (Drew, Goodyear, and Haworth, J., 1927, 1237) that the latter is considerably more stable than the former. The proportions of each found in the epimeric mixture are of the order of 5% of the former and 95% of the latter.

An unexpected result which has developed from this work is the transformation of 2 : 3 : 4-trimethyl δ-xylonolactone into furan-carboxylic acid, which was isolated as the main product of the interconversion.



It is evident that aqueous pyridine is endowed with a remarkable capacity for eliminating methoxy-groups. This reaction is being investigated more closely in order to discover whether the furan-carboxylic acid is preceded by a stage represented by the intermediate formation of a pyrone derivative, since there appears to be some evidence of this.

Meanwhile the above transformation throws some light on the changes which normal pentoses undergo when acted upon by dilute acid to give furfural.

EXPERIMENTAL.

The method adopted to effect the epimerisation of the methylated lactones was to dissolve 2 parts by weight of the lactone in 1 part of pyridine and 14 parts of water (compare Hedenhurg and Cretcher, *J. Amer. Chem. Soc.*, 1927, **49**, 478). The solution was heated in a closed flask on a boiling water-bath during 100—120 hours. Since the solution was usually coloured at this stage, it was clarified with charcoal and diluted with much water. The water and pyridine were then removed by distillation under diminished pressure, and more water was rapidly added and again evaporated until the colourless syrupy residue was free from pyridine. Hydrolysis of the pyridine salt of the organic acid was complete after this treatment. Inasmuch as the procedure followed during the isolation of the products differed for each individual lactone, the details are briefly described in each case.

I. *Conversion of* 2 : 3 : 5 : 6-*Tetramethyl γ-Gluconolactone into* 2 : 3 : 5 : 6-*Tetramethyl γ-Mannonolactone*.—The crystalline tetramethyl gluconolactone, m. p. 26—27·5°, was digested with aqueous pyridine and yielded a syrup which crystallised rapidly. From light petroleum solution (b. p. 80—100°), it separated readily in long transparent needles, m. p. 109°. In admixture with a specimen of 2 : 3 : 5 : 6-tetramethyl γ-mannonolactone the m. p. showed no depression (Goodyear and Haworth, J., 1927, 3136) (Found : OMe, 52·3. Calc., 53·0%).

Further confirmation of the identity of the mannonolactone was obtained by preparing from it the phenylhydrazide of the corresponding acid. This separated from benzene as minute colourless prisms, m. p. 167°. A mixed m. p. determination was made with the specimen described by Goodyear and Haworth (*loc. cit.*) and showed no depression (yield, 60%).

The mother-liquors gave on evaporation a further quantity of the tetramethyl γ-mannonolactone, but the major portion of the residual syrup did not crystallise. This was digested with a proportional amount of phenylhydrazine, and the addition of benzene led to the separation of crystals of a phenylhydrazide, m. p. 134—135°. In admixture with an authentic specimen of the phenylhydrazide of 2 : 3 : 5 : 6-tetramethyl gluconic acid (m. p. 135—136°) (Haworth and Long, J., 1927, 544) there was no depression. This represented the portion of the original gluconolactone which had not been transformed.

II. *Conversion of* 2 : 3 : 5 : 6-*Tetramethyl γ-Mannonolactone into* 2 : 3 : 5 : 6-*Tetramethyl γ-Gluconolactone* (with Dr. E. H. Goodyear).—The procedure followed was identical with that described above under section I. About 50% of the original substance was recovered as the crystalline 2 : 3 : 5 : 6-tetramethyl γ-mannonolactone, and the mother-liquors also contained this unchanged lactone, which was isolated in the form of the phenylhydrazide of the corresponding 2 : 3 : 5 : 6-tetramethyl mannonic acid. The conversion in the direction of the gluconolactone proceeded to the extent of not more than 30%. From the mixture of the phenylhydrazides obtained after the conversion, a quantity of the crystalline phenylhydrazide (m. p. 134—135°) of 2 : 3 : 5 : 6-tetramethyl gluconic acid was isolated. The identity of this product was confirmed by mixed m. p. determination with an authentic specimen (Charlton, Haworth, and Peat, J., 1926, 89; Haworth and Peat, *ibid.*, p. 3100).

III. *Conversion of* 2 : 3 : 4 : 6-*Tetramethyl δ-Gluconolactone into* 2 : 3 : 4 : 6-*Tetramethyl δ-Mannonolactone.*—After treatment of the methylated δ-gluconolactone with aqueous pyridine the syrupy product was heated with phenylhydrazine during ½ hour, and gave a 90% yield of a crystalline substance which, purified from benzene, was identified as the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl mannonic acid, m. p. 184—185° (Found : C, 56·0; H, 7·8; N, 8·4; OMe, 35·6. Calc. : C, 56·1; H, 7·6; N, 8·2; OMe, 36·3%). This gave no depression in admixture with an authentic specimen prepared by Drew, Goodyear, and Haworth (*loc. cit.*). The mother-liquors gave a 5% yield of the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl gluconic acid, m. p. 115°.

IV. *Conversion of 2 : 3 : 4 : 6-Tetramethyl δ-Mannonolactone into 2 : 3 : 4 : 6-Tetramethyl δ-Gluconolactone.*—The product from the pyridine treatment was not crystalline, and was heated for 1 minute with phenylhydrazine. A crystalline phenylhydrazide separated, m. p. 184—185°. This was identified as the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl mannonic acid. The mother-liquors evidently contained the conversion product in the form of the free lactone. These were evaporated and the residue was heated for ½ hour with phenylhydrazine. Crystals again separated, which were purified from ether; m. p. 184°. The major portion of this product was thus the phenylhydrazide from the unchanged δ-mannonolactone. The concentrated mother-liquors, dissolved in ether, deposited another crystalline product, which was purified by recrystallisation (ether) and had m. p. 113—114°. This was identified as the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl gluconic acid by mixed m. p. determination with a specimen prepared by Haworth, Hirst, and Miller (J., 1927, 2436). The conversion in the direction of δ-mannono- to δ-glucono-lactone was not more than 8%.

V. *Conversion of 2 : 3 : 4-Trimethyl δ-Xylonolactone into 2 : 3 : 4-Trimethyl δ-Lyxonolactone.*—The conversion followed the usual course, except that the syrupy product deposited a crystalline substance, which was identified as a furancarboxylic acid, m. p. 131—132° (Found : C, 53·5; H, 3·4%), formed (yield, 63%) through a secondary reaction involving the elimination of methyl alcohol. The remaining syrup was heated with phenylhydrazine containing a little dry ether, and on evaporation of the solvent the corresponding phenylhydrazide crystallised. This was purified from benzene and yielded colourless needles, m. p. 180—181° (Found : C, 56·1; H, 7·3; OMe, 30·6; N, 9·7. Calc. for $C_{14}H_{22}O_5N_2$: C, 56·4; H, 7·4; OMe, 31·2; N, 9·4%). This was identified as the phenylhydrazide of 2 : 3 : 4-trimethyl lyxonic acid—a substance recently prepared from trimethyl lyxose (Hirst and Smith, J., 1928, 3147). A mixed m. p. determination of the phenylhydrazide prepared by the latter method gave no depression. In admixture with a specimen of the *phenylhydrazide* of 2 : 3 : 4-trimethyl δ-xylonic acid, m. p. 137—138·5° (Found : C, 56·5; N, 7·45; OMe, 30·9; N, 9·45. $C_{14}H_{22}O_5N_2$ requires C, 56·4; H, 7·4; OMe, 31·2; N, 9·4%), which was prepared for this comparison from the initial material, the m. p. was depressed.

VI. *Conversion of 2 : 3 : 5-Trimethyl γ-Xylonolactone into 2 : 3 : 5-Trimethyl γ-Lyxonolactone.*—Trimethyl γ-xylonolactone (1 g.) was heated with aqueous pyridine and gave, on concentration of the solution, a coloured syrup. Part of this (0·6 g.) was soluble in ether and gave a *phenylhydrazide* (m. p. 142°) in minute hexagonal

prisms (Found : C, 56·25; H, 7·35. $C_{14}H_{22}O_5N_2$ requires C, 56·4; H, 7·4%).

The conversion into the lyxonolactone had proceeded to the extent of 60% of the total quantity of methylated xylonolactone originally taken.

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UNIVERSITY OF BIRMINGHAM,
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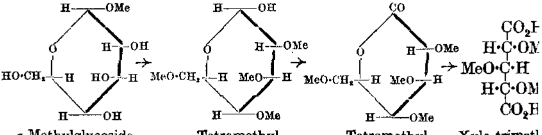
LIII.—*Synthesis of* 1-2 : 3 : 4 : 6-*Tetramethyl* δ-*Glucono-lactone and of* 1-2 : 3 : 4 : 6-*Tetramethyl* δ-*Mannono-lactone from* 1-2 : 3 : 5-*Trimethyl Arabofuranose.*

By WALTER NORMAN HAWORTH and STANLEY PEAT.

THE determination of the ring structure of α- and β-methyl-glucosides and of α-methylmannoside by one of us has hitherto been founded upon their conversion, through tetramethyl gluco-pyranose and tetramethyl mannopyranose, into the δ-lactones, followed by oxidation of these lactones to trimethoxyglutaric acids, *e.g.*,



α-Methylglucoside. Tetramethyl glucopyranose. Tetramethyl δ-gluconolactone. Xylo-trimethoxyglutaric acid.

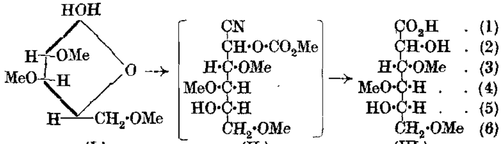
In the present work the *l*-forms of these δ-lactones have been synthetically prepared by a procedure which affords a further confirmation of their constitutional formulæ. This synthetic proof is dependent upon the constitution of the γ-form of *l*-trimethyl arabinose which has previously been determined by methods of oxidation, and the constitution assigned to it is that of trimethyl arabofuranose (I).

The usual method for ascending the sugar series from pentose to hexose involves the addition of hydrogen cyanide, followed by

hydrolysis of the cyanohydrin to the related carboxylic acid, which, by ring closure, is transformed into the lactone and thence by reduction into the next higher member in the sugar series. We have modified this experimental procedure and have condensed a methylated pentose with methyl chloroformate and potassium cyanide. In a preliminary experiment the *normal* trimethyl arabopyranose was condensed with these reagents and gave a crystalline trimethyl carbomethoxy mannononitrile, and also a liquid which contained this crystalline product as well as the correspondingly substituted gluconpremier.

For the particular object which the authors had in view, it was necessary to utilise as the initial sugar the corresponding derivative of γ-arabinose, namely, 2 : 3 : 5-trimethyl arabofuranose (I). This has been made available by the earlier work of Baker and Haworth (J., 1925, **127**, 365). Although it would have been preferable to utilise for this purpose the *d*-sugar, which is, however, almost *inaccessible, nevertheless the same theoretical conclusions could* be reached by working with the natural *l*-arabinose which is readily obtainable.

The above derivative of γ-arabinose (I) condensed easily in the cold with potassium cyanide and methyl chloroformate. The products, a crystalline substance and a liquid, are provisionally represented by the formula (II), although it is not certain whether the carbomethoxy-residue in this mixture of isomeric compounds is situated at position 2 or position 5 in the lengthened carbon chain.

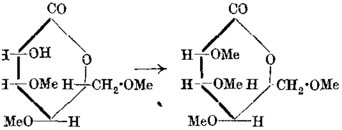


(I.) (II.) (III.)

In either event, the subsequent hydrolysis of both the nitrile and the carbomethoxy-group would give rise to the same pair of stereoisomeric forms of a 3 : 4 : 6-trimethyl hexonic acid (III), in which the hydroxyl at position 2 is directed to the right and to the left, respectively.

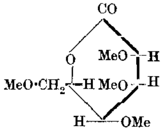
This acid product (III) was converted into the two δ-lactones by heating, and in contact with phenylhydrazine the latter gave the two stereoisomeric crystalline forms of the phenylhydrazides of the acids, which were separated by a tedious fractional crystallisation. The phenylhydrazine residue was subsequently eliminated

from each of the crystalline specimens, and there were thus obtained the two trimethyl-δ-lactones (IV) and (VI). A fourth methyl group was then introduced into each of these compounds and the tetramethyl δ-lactones (V) and (VII) were isolated.

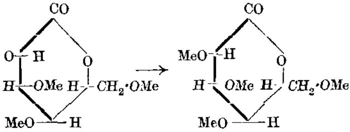


(IV.) *l*-Trimethyl δ-mannonolactone.

(V.) *l*-Tetramethyl δ-mannonolactone.

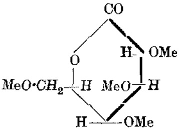


(VIII.) *d*-Tetramethyl δ-mannonolactone.



(VI.) *l*-Trimethyl δ-gluconolactone.

(VII.) *l*-Tetramethyl δ-gluconolactone.



(IX.) *d*-Tetramethyl δ-gluconolactone.

The pair of completely methylated lactones (V) and (VII) were condensed with phenylhydrazine and thereby converted into the crystalline *phenylhydrazides* of the *l*-2 : 3 : 4 : 6-*tetramethyl mannonic* and *gluconic acids*. These were found to be identical in m. p. and rotation with the enantiomorphous compounds prepared from the δ-lactones (VIII) and (IX), except that the signs of their optical rotation were opposite. The latter two are the members of the *d*-series of δ-lactones which have been fully investigated in earlier experiments and are prepared respectively from α-methylmannoside and α- and β-methylglucosides (Drew, Goodyear, and Haworth, J., 1927, 1237; Goodyear and Haworth, *ibid.*, p. 3136; Haworth, Hirst, and Miller, *ibid.*, p. 2436).

l-Series (synthetic).	*d*-Series.
Phenylhydrazide from	Phenylhydrazide from
l-2 : 3 : 4 : 6-tetramethyl δ-mannonolactone :	*d*-2 : 3 : 4 : 6-tetramethyl δ-mannonolactone :
m. p. 183—184°, $[\alpha]_D^{16°}$ +22°.	m. p. 183—184°, $[\alpha]_D^{16°}$ −22°.
l-2 : 3 : 4 : 6-tetramethyl δ-gluconolactone :	*d*-2 : 3 : 4 : 6-tetramethyl δ-gluconolactone :
m. p. 115°, $[\alpha]_{5780}^{19°}$ −50°.	m. p. 115°, $[\alpha]_{5780}^{19°}$ +50·8°.

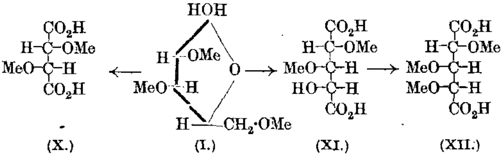
A further comparison was established between the *l*- and *d*-forms of the tetramethyl mannonolactones themselves. Thus it was

found that the synthetic *l*-2 : 3 : 4 : 6-*tetramethyl δ-mannonolactone* showed $[\alpha]_D^{18°}$ −150° (initially) ⟶ − 58° (after 150 hours), whilst the specimens of the *d*-lactone, which had previously been prepared from *d*-2 : 3 : 4 : 6-tetramethyl *d*-mannose, gave $[\alpha]_D^{18°}$ + 150° ⟶ + 63° (after 150 hours).

The synthetic *l*-forms are thus seen, by their mode of synthesis, to be constituted as six-atom ring compounds (the manno- and gluco-pyranolactones), a conclusion which verifies the structure assigned to the two *d*-compounds on the basis of their degradative oxidation to arabo-trimethoxyglutaric acid and to xylo-trimethoxyglutaric acid respectively.

This synthesis confirms the conclusions already reached in the constitutional study of γ- and normal sugars inasmuch as it is seen that these two types stand in the relation to each other as five-atom ring compounds and six-atom ring compounds. The furanose type has thus been transformed into the pyranose type by a procedure which admits only of the formation of a six-membered ring.

The starting point in the synthesis is represented by a trimethyl sugar to which a constitution has been assigned on the ground of its degradative oxidation. Thus the trimethyl arabofuranose (I) has been degraded by oxidation to give *d*-dimethoxysuccinic acid (X), which is characterised as the crystalline methylamide and amide (Haworth, Hirst, and Learner, J., 1927, 2432). The trimethyl arabofuranose has also been oxidised to hydroxydimethoxyglutaric acid (XI) which, on further methylation, passes into the *l*-arabo-trimethoxyglutaric acid (XII) (Baker and Haworth, *loc. cit.*; Haworth and Nicholson, J., 1926, 1899). The latter product has been identified through its crystalline amide :



(X.) (I.) (XI.) (XII.)

Incidentally, it may be remarked that the syntheses now recorded have furnished an alternative proof that the conclusions reached by C. S. Hudson on the ring structure of α- and β-methylglucosides are invalid (compare Haworth and Hirst, J., 1928, 1221). By the use of a statistical method involving an extension of the principle of optical superposition, Hudson concluded that α-methylglucoside contained a 1 : 4-oxide ring, and α-methylmannoside a 1 : 5-oxide

ring. Although this view has been given some currency, it should finally be set aside.

EXPERIMENTAL.

I. *Condensation of* 1-2 : 3 : 4-*Trimethyl Arabopyranose with Hydrogen Cyanide and Methyl Chloroformate. Formation of* 3 : 4 : 5-*Trimethylcarbomethoxy Glucono- and Mannono-nitriles.*—This method for the ascent of the sugar series was devised for the reasons stated in the introduction.

2 : 3 : 4-Trimethyl arabinose (trimethyl arabopyranose) was prepared by methylation of the normal methylarabinosides. The trimethyl sugar (7·6 g.) was dissolved in 40 c.c. of water containing 2·7 g. of potassium cyanide and to this were added, in three portions, 3·1 c.c. of methyl chloroformate, the mixture being cooled in ice and shaken vigorously. The solution separated into two layers, and after 1 hour was extracted three times with chloroform. These extracts were washed repeatedly with water, dried, and evaporated, and yielded a viscid, colourless syrup (7·5 g.) which partly crystallised. The separated solid was obtained from ether–light petroleum (b. p. 40—60°) as colourless needles, m. p. 100—102° (Found : C, 47·6; H, 7·1; N, 5·1; OMe, 43·1. $C_{11}H_{19}O_7N$ requires C, 47·6; H, 6·9; N, 5·1; OMe, 44·8%). Both the crystalline and the syrupy product had the following properties: they reduced Fehling's solution only after boiling for 5 minutes; in solution they gave a heavy precipitate of barium carbonate on addition of barium hydroxide, and, on boiling, ammonia was evolved. In other respects also they appeared to be similar. The liquid product was a mixture of substituted *l*-glucono- and *l*-mannono-nitriles, whereas the crystalline substance was evidently one of these substances, probably the mannononitrile, which had separated by crystallisation.

The liquid specimen of the nitrile was not very stable and showed a tendency to deteriorate on keeping.

II. *Condensation of* 1-2 : 3 : 5-*Trimethyl Arabofuranose with Hydrogen Cyanide and Methyl Chloroformate. Formation of* 1-3 : 4 : 6-*Trimethylcarbomethoxy Glucono- and Mannono-nitriles.*—This condensation was carried out in the manner described above for the trimethyl arabopyranose. γ-Methylarabinoside was methylated by methyl sulphate to the trimethyl γ-methylarabinoside, and by hydrolysis the 2 : 3 : 5-trimethyl γ-arabinose (or trimethyl arabofuranose) was isolated (Baker and Haworth, *loc. cit.*; Haworth, Hirst, and Learner, J., 1927, 2432). The latter sugar (1 mol.) was dissolved in ice-cold water containing potassium cyanide (1 mol.), methyl chloroformate (1 mol.) added in small quantities, and the mixture shaken vigorously in a stoppered bottle. After being kept for 2 hours at 5°, the solution separated into two layers, the

lower layer being soluble in chloroform. The chloroform extract was washed with water, dried over magnesium sulphate, and evaporated. This gave a viscid orange syrup which did not crystallise (yield, 84% of the theoretical). Towards reagents it exhibited a behaviour similar to that of the product from trimethyl arabopyranose described under section (I).

There was indeed little douht that the syrup was a mixture of *l*-3 : 4 : 6-trimethyl-2-carbomethoxy glucono- and mannono-nitriles. It was somewhat unstable, showing a tendency to lose hydrogen cyanide on keeping, and it was therefore hydrolysed at once to the corresponding acid.

III. l-3 : 4 : 6-*Trimethyl Gluconic and Mannonic Acids.*—The above nitrile was hydrolysed in two stages as follows. It was dissolved in ether and filtered from a small residue of white solid, and hydrogen chloride was passed into the well-cooled filtrate. The solution formed two layers and the admission of hydrogen chloride was continued until a homogeneous solution was again obtained. On removal from the cooling bath the solution deposited ammonium chloride. On the next day more hydrogen chloride was admitted and the solution was kept for 3 more days. The ether and hydrogen chloride were removed by aeration and by keeping in a vacuum over solid potassium hydroxide. The product was a mixture of a syrupy organic acid and ammonium chloride. A chloroform extract of the residue was taken, and traces of hydrogen chloride were removed from it by agitation with very little silver carbonate. Evaporation of the filtered solution gave a dark syrup and left a slight residue insoluble in ether. The ethereal solution was treated with charcoal and evaporated; the pale yellow syrup obtained crystallised but not completely. The crystals, m. p. 155°, gave analytical figures corresponding with 1-2-*carbomethoxy*-3 : 4 : 6-*trimethyl mannonic acid* (Found: C, 44·6; H, 6·9. $C_{11}H_{20}O_9$ requires C, 44·6; H, 6·8%). The crystals and syrup, which evidently still contained carbomethoxy-residue, were further hydrolysed by digestion with *N*/3-barium hydroxide, and the organic acid was recovered from the barium salt. It was now distilled under 0·05 mm. pressure from a bath heated at 150—180° and obtained in the form of its lactone. The crystalline acid similarly gave a colourless lactone on heating.

Since separation of the stereoisomeric acids or lactones could not readily be achieved by direct means, the latter were heated for a few minutes with molecular quantities of phenylhydrazine. On the addition of benzene the product crystallised at once, m. p. 111—127°.

By repeated fractional crystallisation from benzene the stereoisomeric phenylhydrazides of the 3 : 4 : 6-trimethyl gluconic and

mannonic acids were separated. The less soluble *phenylhydrazide* (A), m. p. 137—139°, was shown to be the mannono-compound. The corresponding glucono-compound (B) melted, though not sharply, at 125° and probably still retained a trace of (A) [Found for (A): C, 54·7; H, 7·5; N, 8·8; OMe, 28·6. $C_{15}H_{24}O_6N_2$ requires C, 54·8; H, 7·7; N, 8·5; OMe, 28·35%]. The phenylhydrazide (A) was hydrolysed at 90° with *N*/10-hydrochloric acid (in slight excess), the water evaporated at 35°, and the residue dried. Evaporation of the dry ethereal extract from this product yielded a viscid syrup which crystallised in hard colourless prisms, m. p. 96—97°, from ether (Found: C, 49·1; H, 7·5; OMe, 41·8. $C_9H_{16}O_6$ requires C, 49·1; H, 7·5; OMe, 42·3%). Further experiments proved this compound to be 1-3 : 4 : 6-*trimethyl* δ-*mannonolactone*. It showed the following polarimetric values in water (c = 1·88).

Hours ...	0	½	1½	5	9	22	34	74
$[\alpha]_D$	−167°	165^{5}	161·8°	155·2°	147·2°	126·5°	119°	112·8° (constant)

An attempt was made to reduce this lactone to the sugar with sodium amalgam, but the slowness of the reaction would have required the use of more material than was available, and this part of the work was postponed.

IV. 1-2 : 3 : 4 : 6-*Tetramethyl* δ-*Mannonolactone*.—The methylation of the crystalline 3 : 4 : 6-trimethyl mannonolactone was achieved by using silver oxide and methyl iodide which had been specially dried. The product, which had partly crystallised (Found: OMe, 50·8%), distilled as a colourless oil. This was heated with phenylhydrazine (equal mols.) along with a little ether, and as soon as the ether evaporated the residue crystallised to a hard cake, which was purified to give needles, m. p. 183—184° (Found: C, 55·75; H, 7·55. Calc.: C, 56·1; H, 7·6%). This *l*-phenylhydrazide showed $[\alpha]_D^{16°}$ +22° (c = 1·37 in chloroform), whereas the corresponding *d*-isomeride prepared by Haworth and Long (preceding paper) showed −22° (c = 1·37).

The above phenylhydrazide was hydrolysed and the tetramethyl mannonic acid converted into the lactone, which was distilled under 0·06 mm. from a bath at 145—150°. The liquid lactone crystallised to a low-melting solid (the *d*-isomeride has m. p. 23—25°) and showed, in water, $[\alpha]_D^{16°}$ −150° (¼ hour), −95·6° (28 hours), −69·4° (98 hours), −58·2° (150 hours) constant. The *d*-2 : 3 : 4 : 6-tetramethyl δ-mannonolactone prepared by Drew, Goodyear, and Haworth (*loc. cit.*) showed $[\alpha]_D^{18°}$ +150° ⟶ +63° (after 146 hours).

The slightly impure phenylhydrazide (B, above) of 3 : 4 : 6-trimethyl gluconic acid was hydrolysed in the usual manner with *N*/10-hydrochloric acid. After extraction the liberated organic

acid was heated at 100°, and its ethereal solution treated with charcoal and evaporated. The resulting lactone showed $[\alpha]_D$ $-90°$ changing to $-27°$ in aqueous solution after 30 hours ($c = 1·6$).

The trimethyl lactone was now methylated by Purdie's reagents, and the liquid tetramethyl lactone was distilled from a bath at 115°/0·5 mm. The distillate was a colourless liquid. This was digested with phenylhydrazine and gave almost immediately colourless crystals which were purified first from benzene and then from ether. A small quantity of the above *l*-2 : 3 : 4 : 6-tetramethyl mannonophenylhydrazide separated, m. p. 183—184°, and this was followed by the separation from the solution of the *l*-2 : 3 : 4 : 6-*tetramethyl gluconophenylhydrazide*, m. p. 115° (Found for the latter: C, 55·8; H, 7·5; OMe, 36·3. $C_{16}H_{26}O_6N_2$ requires C, 56·1; H, 7·6; OMe, 36·3%).

The phenylhydrazide of *l*-2 : 3 : 4 : 6-tetramethyl gluconic acid showed $[\alpha]_{5780}^{19°}$ $-50°$ in ethyl alcohol, which compares with the value $[\alpha]_{5780}^{19°}$ $+50·8°$ obtained for the corresponding *d*-enantiomorph.

The authors are indebted to the Department of Scientific and Industrial Research for the award of a research assistantship to one of them (S. P.), and to the Government Grant Committee of the Royal Society for a grant which has contributed towards the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, January 7th,* 1929.]

NOTES.

Some Derivatives of Tri-p-*tolylsilicane.* By ALFRED RAYMOND STEELE and FREDERIC STANLEY KIPPING.

THE distillation of the crude product of the interaction of silicon tetrachloride and magnesium *p*-tolyl bromide (Pink and Kipping, J., 1923, **123**, 2832) gives a considerable fraction collected from about 250° to 300° which deposits crystals in the course of several weeks; when separated by filtration and recrystallised from hot light petroleum, this solid gives *tri*-p-*tolylsilicyl chloride*, $Si(C_7H_7)_3Cl$, in colourless rhomboidal prisms, m. p. 115—116° (Found: Cl, 10·8. $C_{21}H_{21}ClSi$ requires Cl, 10·5%). The chloride is readily soluble in most of the common solvents; it does not fume appreciably on exposure to moist air and is only slowly decomposed by cold water.

Tri-p-*tolylsilicol*, $Si(C_7H_7)_3·OH$, was prepared by treating the chloride with a dilute solution of ammonium hydroxide in aqueous

acetone. It separates from light petroleum in compact lustrous crystals, apparently octahedra, m. p. 99—100° (Found: Si, 8·8. $C_{21}H_{22}OSi$ requires Si, 8·8%). It is very readily soluble in chloroform, benzene and acetone, but much less so in cold light petroleum or alcohol.

Tri-p-*tolylsilicyl oxide*, $[Si(C_7H_7)_3]_2O$, is obtained when an alcoholic solution of the silicol containing a few drops of a 10% solution of sodium hydroxide is evaporated on the water-bath, and the residue heated during about an hour. It crystallises well from chloroform–acetone in rhomboidal plates, m. p. 223—224° (Found: Si, 9·2. $C_{42}H_{42}OSi_2$ requires Si, 9·15%). It dissolves freely in chloroform and fairly readily in benzene, but is only sparingly soluble in light petroleum and acetone.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 9th*, 1929.]

The Influence of Colloids on the Precipitation of Salts. By ROBERT DICKINSON.

PREVIOUS workers (Williams and Mackenzie, J., 1920, **117**, 844; Bolam and Mackenzie, *Trans. Faraday Soc.*, 1926, **22**, 151, 162; Bolam and Desai, *ibid.*, 1928, **24**, 50; Bolam, *ibid.*, p. 463) have shown that silver chromate and lead iodide can be maintained in supersaturated solutions by the presence of gelatin and of agar-agar respectively.

A striking example of the above phenomenon has now been observed in the case of *lead sozoiodolate* (3 : 5-*di-iodo*-4-*hydroxybenzenesulphonate*) [Found: Pb, 30·6, 30·3. $C_6H_2O_4I_2SPb$ requires Pb, 32·8. $(C_6H_3O_4I_2S)_2Pb$ requires Pb, 19·6%], in which sozoiodol acts as a dibasic acid. The low values for lead are probably due to partial volatilisation of lead iodide.

When equivalent solutions of lead acetate and sodium sozoiodolate were mixed to give a volume of 50 c.c. containing 0·5% Pb, no change was observed for about 10 seconds. Nuclei then appeared, and these rapidly increased in size and number until the liquid finally became a semi-solid mass of minute lemon-yellow needles. The amount of precipitate was 0·5058 g. (calc., 0·762 g.), hence the solubility of lead sozoiodolate in water is 0·512 g. per 100 c.c. of solution.

On repeating the above experiment, but having 2% of gum acacia also present in the solution, no change was observed for at least 2 hours. Minute yellow nodules then appeared on the bottom of the flask and slowly increased in size; they were not numerous (less than 100), and some attained a diameter of nearly 1 mm. When equilibrium had been reached, the weight of solid was found

to be 0·204 g., and hence the solubility of lead sozoiodolate in 2% gum acacia solution is 1·116 g. per 100 c.c. of solution. Thus gum acacia prevents the precipitation of more than half the expected amount of this lead salt.

The behaviour of gelatin in this connexion could not be studied, since it reacts with sodium sozoiodolate to give a white rubber-like precipitate; and despite an extensive examination of many other lead salts, no further example of this phenomenon has been observed.

This work was carried out on behalf of the Liverpool Medical Research Organisation.—THE UNIVERSITY, LIVERPOOL. [*Received, November 22nd*, 1928.]

On the Individuality of Humulene. By A. CHASTON CHAPMAN.

IN his reply to my paper entitled " On the Individuality of Humulene " (J., 1928, 785) Deussen (*J. pr. Chem.*, 1928, **120**, 133) gives certain tables illustrating the fractional distillation of specimens of caryophyllene, and shows the relation between the boiling ranges, optical rotations and yields of nitrosochloride, nitrosite and nitrosate. His results are not altogether easy to understand, but so far as they go they are quite consistent with the presence in the caryophyllene of a proportion of humulene.

I may incidentally point out two instances in which Deussen has evidently misunderstood me. In my paper I stated that the 5 lb. of caryophyllene with which I actually worked was a portion of 40 lb. of the crude hydrocarbon itself, and not, as Deussen appears to have thought, of clove oil.

In the second place, I need scarcely say that I made a large number of fractional distillations (not two, as stated by Deussen), using in the end, for the purposes of my examination, the two fractions which differed most widely in their boiling points.

Both Deussen's results and mine appear to indicate very clearly that the inactive hydrocarbon which is present in clove oil is, in fact, identical with the hydrocarbon which I obtained in 1895 from hop oil, and to which I gave the name " humulene." That this hydrocarbon is not caryophyllene is shown by the fact that it does not yield a crystalline alcohol, and further that its nitrosite differs from that of caryophyllene. There need be no confusion in nomenclature such as that to which Deussen refers, and in any case it does not constitute an argument of any weight, and may be disregarded.

In conclusion, no inactive hydrocarbon having all the properties of caryophyllene has ever been obtained, and I see no reason to modify the view I have always held—and which has been confirmed by

others—that humulene is not identical with caryophyllene. In the terpene series identity of derivatives is by no means to be regarded as definite evidence of the identity of the parent hydrocarbons. On the other hand, differences in behaviour in respect of the formation of derivatives is strong evidence that the parent hydrocarbons are not the same. It is tolerably clear that humulene and caryophyllene are closely related, and it is not impossible that in certain reactions intramolecular change occurs, the one being transformed into the other.—CHEMICAL LABORATORIES, 8, DUKE STREET, E.C. 3. [*Received, January 18th, 1929.*]

LIV.—*Organic Derivatives of Silicon. Part XXXVIII. The Formation of Tri- and Tetra-phenylsilicane and Complex Synthetical Products from Octaphenyl*cyclo*silicotetrane.*

By FREDERIC STANLEY KIPPING and ARTHUR GEORGE MURRAY.

BY the " distillation " of the glue-like substance (E) which is formed by the action of sodium on diphenylsilicon dichloride there was obtained a small proportion of a thick oil; this product, on oxidation, gave triphenylsilicol, and with acetone and alkali it gave hydrogen and triphenylsilicol; the weight of the triphenylsilicyl oxide obtained from the silicol was at least 80% of that of the crude oil (Kipping, J., 1927, 2726).

It was evident from these facts that this product contained $SiPh_3$– groups, but, as it had been formed in small quantities only from crude material, in which there might have been unsuspected impurities, its origin and its nature remained unknown.

Other results of the investigation of (E) having led to the conclusion that this amorphous substance is merely a physically different form of octaphenyl*cyclo*silicotetrane (B), it seemed to follow that crystalline (B) should also give a decomposition product from which triphenylsilicol could be obtained under the conditions already mentioned.

This deduction was proved to be a sound one: when pure octaphenyl*cyclo*silicotetrane is strongly heated in the absence of air, it yields a thick colourless oily distillate and a pale yellow resinous residue; towards the end of the operation a little frothing occurs, but there is no charring. The distillate soon deposits crystals of tetraphenylsilicane, mixed, usually with some (B); when freed from these sparingly soluble compounds, the product is a colourless oil which seems to be almost quantitatively transformed into triphenyl-

silicol with evolution of hydrogen when it is treated with piperidine and alkali.

The results of combustions, silicon determinations and cryoscopic measurements in benzene solution seemed to show that the oil was triphenylsilicyl, $SiPh_3$, but, although it readily reduced potassium permanganate, it did not combine with iodine and when treated with a very small proportion of bromine in chloroform solution it immediately gave hydrogen bromide. Further, the hydrogen value (J., 1921, **119**, 848) of the oil did not agree with that required for *triphenylsilicyl*: $2SiPh_3 + 2H_2O = 2SiPh_3{\cdot}OH + H_2$ (hydrogen value = 42·9) but was in close accordance with that calculated for *triphenylsilicane*: $SiPh_3H + H_2O = SiPh_3{\cdot}OH + H_2$ (hydrogen value = 85·4).

Now a crystalline substance to which he gave the formula of triphenylsilicane was obtained by Ladenburg (*Ber.*, 1907, **40**, 2278) by heating triphenylsilicyl bromide with zinc ethyl and a little benzene in a sealed tube at 120°. This product was sparingly soluble in cold acetone or benzene and melted at 200—203°; the formula assigned to it was based on the results of one combustion and the percentage of silicon in it was not determined. Apart from the fact that the properties of this crystalline substance are hardly those which would be expected of a triphenylsilicane (compare footnote, p. 364), Ladenburg himself states that on repeating his experiments many times, although he endeavoured to keep the conditions the same as before, he obtained almost exclusively the normal product triphenylethylsilicane, which melted at 72—74° and was very readily soluble in acetone or benzene.

It is suggested, therefore, that Ladenburg's substance (m. p. 200—203°) cannot have been triphenylsilicane; the purity of his triphenylsilicyl bromide is not emphasised and his product may have been impure tetraphenylsilicane, as it was from this substance that the bromide had been prepared.*

Discounting the difficulty raised by Ladenburg's statements, it is concluded that the oil from octaphenyl*cyclo*silicotetrane is in fact triphenylsilicane, and the properties of the residue from the distillation may next be considered. This product contains about 20% of silicon, which corresponds approximately with that required for the ratio 2Si : 3Ph. With the aid of solvents it can be separated into fractions having graded properties, some of which have molecular weights probably exceeding 4000.

* In the same paper Ladenburg describes a barium salt of triphenylsilicolsulphonic acid, which, as previously shown (Kipping and Martin, J., 1909, **95**, 489), was in all probability a mixture of silica and barium salts of benzene-mono- and -di-sulphonic acids.

The largest fraction, a colourless granular powder, combines with only a very small proportion of iodine and seems therefore to contain a correspondingly small proportion of ter- (or bi-) valent silicon atoms. Its hydrogen value is considerably lower than that of $(SiPh_2)_4$, whereas the mere elimination of $SiPh_4$ or $SiPh_3$– groups from that compound should give a product of enhanced hydrogen value.

When this largest fraction is treated with alkali and piperidine, only a small proportion is converted into compounds soluble in aqueous solutions of alkali, and diphenylsilicanediol could not be detected in these solutions; whether the portion insoluble in alkalis consists of unchanged substance or of condensation products of substituted silicols could not be definitely determined.

From the available evidence it must be presumed that in addition to the fission of Si–Si bindings and the migration of phenyl groups from one silicon atom to another, giving $SiPh_4$ and $SiPh_3$–, many other changes occur during the "distillation" of (B). It may therefore be suggested that $-SiPh_2-SiPh_2-$ complexes may be converted into $-Si{<}^{C_6H_4}_{C_6H_4}{>}Si-$ with liberation of hydrogen, which combines with the $SiPh_3$– groups to form triphenylsilicane; the low hydrogen value of the residue and its apparent freedom from $>SiPh_2$ groups may possibly be due to a somewhat similar transformation of $-SiPh_2-SiPh_2-$ into $-SiPh{<}^{C_6H_4}_{C_6H_4}{>}SiPh-$ with fission of the Si–Si linkage. The complex character of the residue and the small quantities available, but more particularly the lack of known methods for attacking such problems, render it impossible to put these suggestions to the test of experiment; or to ascertain whether the production of the compounds of high molecular weight from the fragments of Si_4Ph_8 is due to combination between silicon and silicon, carbon and carbon, or carbon and silicon.

Octaphenylsilicotetraue (A), when strongly heated, also gives triphenyl- and tetraphenyl-silicane and it is of interest to note that this open-chain compound seems to yield none of its cyclic isomeride under these conditions; nor does the latter give any octaphenylsilicotetrane.

EXPERIMENTAL.

*Destructive Distillation of Octaphenyl*cyclo*silicotetrane.*—The pure compound (1·5—2 g.) is placed in a very small distillation flask having a short (1—1½") neck and the air in the flask and receiver is displaced by dry nitrogen: the flask is then heated in a metal bath in which it is immersed so far as possible, the delivery tube being pointed downwards almost vertically. When a 5" flame of an ordinary Bunsen is used for heating the bath, the solid in the

flask shows signs of sintering after the expiration of about 5 minutes and shortly afterwards most of it has melted; at the end of about 6 minutes oily drops appear above the molten layer and a colourless oil begins to collect in the receiver, but only very slowly. After 12—15 minutes time from the start of the operation the residue has turned faintly yellow and the apparent ebullition ceases, giving place to a slight frothing; at this stage the heating is stopped. No thermometer is used, but, as the octaphenyl compound only melts above 400°, it is probable that the temperature of the bath was above 450°; if the "distillation" is carried out under very low pressure, most of the octaphenyl*cyclo*silicotetrane sublimes and apparently there is little decomposition.

The distillate, which is approximately 40% of the material used, deposits colourless crystals either almost immediately or after the expiration of some hours; the quantity of this deposit seems to depend on the rapidity with which the operation has been conducted, a larger proportion of the cyclic compound passing over unchanged the more quickly it is heated. The distillate is mixed with 10—15 vols. of light petroleum and after it has been kept at 0° during some hours the solution is filtered. The crystalline residue fractionated from a mixture of chloroform and benzene gives well-defined pointed prisms, melting at 235—236°: this compound was identified as tetraphenylsilicane by direct comparison in various ways and by mixed melting point determinations. The mother-liquors from the tetraphenyl derivative give deposits which, fractionated from benzene and acetone, afford pure octaphenyl*cyclo*silicotetrane; this compound was identified by direct comparison and by heating it alone and mixed with a known sample on fusible metal, when both powders sintered and sublimed simultaneously.

During the separation of the tetraphenylsilicane from the cyclic compound microscopic examination revealed the presence, in some deposits, of a few large compact crystals; these proved to be an unusual form of tetraphenylsilicane, quite different from the slender pointed prisms ordinarily obtained. Both forms are often produced together by the slow evaporation of a benzene–chloroform solution, but from carbon tetrachloride at the ordinary temperature tetraphenylsilicane separates in rather ill-defined dome-shaped crystals and in rectangular, almost square, prisms the surfaces of which are deeply pitted.

Formation of Hexaphenylsilicoethane from Silicon Tetrachloride.— On comparing the crystals of the tetraphenylsilicane from octaphenyl*cyclo*silicotetrane with a sample of the tetraphenyl derivative which had been obtained by the interaction of silicon tetrachloride, chlorobenzene, and sodium (Kipping and Lloyd, J., 1901, **79**, 449) the

deposits of the latter, from cold carbon tetrachloride, showed, under the microscope, the presence of some perfect transparent regular hexagons, some of which became black and opaque at 100°; these highly characteristic crystals were proved by direct comparison to be identical with those of hexaphenylsilicoethane, prepared by heating triphenylsilicyl chloride with sodium. The presence of this hexaphenyl derivative in the crude tetraphenylsilicane from the tetrachloride had been long suspected, as the percentage of silicon in the crude product was rather too high; after this lapse of time it is impossible to say definitely that the silicon tetrachloride (Kahlbaum's) was free from the hexachloride, but it seems very probable that this was so, and that the hexaphenyl derivative was formed from the former rather than from the latter.

Triphenylsilicane.—The light petroleum solution of the product of distillation (see above), when evaporated, gave a colourless oil which was freed from solvent uuder reduced pressure and then at 100°; it did not solidify at 0°.* Various samples thus prepared were analysed without further purification; it is very unlikely that they contained more than traces of tetraphenylsilicane or octaphenyl*cyclo*silicotetrane, both of which are practically insoluble in light petroleum; but from the results the presence of a very small proportion of diphenylsilicane is not excluded (Found: C, 81·6; H, 6·1; † Si, 11·3, 11·1; *M*, cryoscopic in benzene, 265; hydrogen value, 84·2, 85·0. $SiPh_3H$ requires C, 83·0; H, 6·1; Si. 10·8%; *M*, 260; hydrogen value, 85·4).

Triphenylsilicane has no appreciable smell, but when heated at 100° it has a slight odour recalling that of diphenyl. It is miscible with all the common solvents except the lower alcohols and acetic acid, in which it is only very sparingly soluble in the cold. When heated in a test-tube over a free flame, it puffs and a pale blue flame passes down the tube, a slight deposition of carbon taking place. It does not decolorise a dilute chloroform solution of iodine at the ordinary temperature, but when the solvent is evaporated and the

* From the following it would seem that the melting point of triphenylsilicane is lower than that of triphenylmethane:

Tetraphenylsilicane	235°	Triphenylsilicyl chloride	90—91°
Tetraphenylmethane	285	Triphenylmethyl chloride	108—111
Triphenylsilicol	148	Triphenylsilicane	oil
Triphenylcarbinol	165	Triphenylmethane	92°
Triphenylsilicyl bromide	118		
Triphenylmethyl bromide	152		

† In the first combustion the oil in the boat was mixed with copper oxide, as the substance seemed to be rather explosive; a very sudden decomposition occurred and the results (C, 80·9; H, 6·0%) were low; in the second combustion copper oxide was not added and the oil, heated very cautiously, decomposed quietly.

residue is heated on a water-bath with excess of the halogen, hydrogen iodide is freely evolved and an oil, probably iodobenzene, volatilises. Treated with a dilute solution of bromine in chloroform, the compound gives an immediate evolution of hydrogen bromide; after the addition of slightly less than one mol. of the halogen and evaporation of the solvent, there remains an oil which, mixed with light petroleum, gives colourless prisms, m. p. 114—118°. This product is doubtless triphenylsilicyl bromide (m. p. 118°); decomposed with aqueous acetone, it yields hydrogen bromide and triphenylsilicol; the latter was identified by means of a mixed melting point determination, etc. Triphenylsilicane is readily oxidised by nitric acid in acetic acid solution, giving triphenylsilicol; it reduces a dilute solution of permanganate in acetic acid at the ordinary temperature.

The most conclusive evidence that the oil is triphenylsilicane is obtained by studying quantitatively its behaviour towards alkalis. It is decomposed by a 5% solution of potassium hydroxide in aqueous acetone at the ordinary temperature with evolution of hydrogen and after some time, if the proportion of acetone is small, triphenylsilicol separates in crystals. When the whole of the acetone has been expelled and the filtered alkaline solution is acidified, there is no precipitation of diphenylsilicanediol: this fact shows that the compound is practically free from $>SiPh_2$ groups. The crystalline residue of triphenylsilicol, when evaporated with alcohol containing a small proportion of potassium hydroxide, and then heated at 100° for some time, becomes only partly soluble in cold alcohol and by repeated treatment a large proportion of the original product of hydrolysis is transformed into triphenylsilicyl oxide. This compound separates from benzene in very lustrous, well-defined, transparent, rhomboidal crystals which become opaque slowly on exposure to the air, rapidly when heated at 100°.* The hydrogen values given above were obtained by treating the oil with piperidine and an aqueous solution of potassium hydroxide and heating gently to complete the decomposition.

Other Decomposition Products.—The residue from the destructive distillation of octaphenyl*cyclo*silicotetrane, when cold, is a brittle resin having the colour of pale honey. Treated with cold chloroform, a small proportion separates in the form of yellow flakes, which have probably been produced from the most strongly heated portions of the material and form only about 4% of the original silicohydrocarbon. This gelatinous product is insoluble in all the

* The statement by Kipping and Lloyd (J., 1901, **79**, 455) that this oxide is "very soluble in ether and benzene" is misleading and should have been "much *more soluble in ether and benzene*"; *its solubility in cold benzene* is less than 1 part in 40.

common solvents, even in boiling aniline; it chars, without melting, at a high temperature and contains 20·2% of silicon, a quantity which corresponds roughly with that required for 2Si : 3Ph. It does not combine with iodine. With an aqueous acetone solution of potassium hydroxide it gives hydrogen very readily, but only a small proportion dissolves even on prolonged heating; the alkaline solution, freed from acetone and filtered, gives with acids an immediate precipitate which is gelatinous and seems to be free from diphenylsilicanediol.

The yellowish chloroform filtrate from the yellow flakes, mixed with acetone, gives a colourless precipitate. The product thus obtained from the combined chloroform solutions from several preparations was again dissolved and precipitated, these operations being repeated systematically many times; four fractions of graded solubility were thus obtained.

Fraction I. The most sparingly soluble portion, which formed about 50% of the total material, was a colourless, apparently amorphous powder which charred at a very high temperature without melting; it contained 20·1% of silicon (2Si : 3Ph requires Si, 19·6%). In chloroform solution it combined with about one-tenth of its weight of iodine, a fact which indicates the presence of some tervalent silicon atoms. It was readily soluble in chloroform and benzene, but practically insoluble in alcohol and acetone. It dissolved completely in a mixture of piperidine and an aqueous solution of potassium hydroxide and gave a hydrogen value of 108, but on the addition of water after the hydrogen evolution had ceased a very considerable precipitate was obtained and the filtered solution gave only a slight gelatinous deposit on the addition of excess of acid. It also gave hydrogen when it was heated with a solution of potassium hydroxide in aqueous acetone, but only a small portion dissolved in the course of some hours; after evaporating the organic solvent and acidifying the filtered solution, there was obtained a gelatinous precipitate which seemed to be free from diphenylsilicanediol; the matter insoluble in aqueous alkali was treated again several times in the same way, but although a little more of it became soluble after each operation, it was not completely hydrolysed at the end of some 30 hours.

From these observations it was possible that the low hydrogen value of this product was due to the presence of some compounds which are not attacked, or only very slowly attacked, by alkali, and attempts to isolate this stable material were therefore made. The powder was dissolved in piperidine and the solution heated with concentrated alkali until the hydrogen evolution ceased; excess of water was then added and the precipitate separated, washed and

dried. It contained 14·4% of silicon and therefore probably consisted of some diphenylsilicane or diphenylenesilicane derivative ($SiPh_2O$ requires Si, 14·1%), but as it seemed to be a mixture and separated from solvents in a glue-like form, its nature could not be determined. So far as could be ascertained, this "glue" was not a component of the original material but had been formed by hydrolysis; if so, it may possibly contain condensation products of

$$(HO)_2Si{<}{}^{C_6H_4}_{C_6H_4}{>}Si(OH)_2.$$

Fraction II was more gelatinous than I; it charred without melting and its molecular weight in camphor was found to be 4800, but the result was probably rather too high, as a clear solution was not obtained.

Fraction III was still more gelatinous; it melted at a high temperature (heated on a spatula) before it charred and its molecular weight in camphor was found to be 1800, a value which is probably trustworthy.

Fraction IV was of a glue-like character; it melted indefinitely below 250° and was slightly soluble in hot acetone.

Decomposition of Octaphenylsilicotetrane.—When this open-chain compound (A) is heated under as nearly as possible the same conditions as those used in the case of its cyclic isomeride, it gives approximately the same proportion of an oily distillate which is a mixture of unchanged (A), tetraphenylsilicane, and a substance miscible with cold light petroleum. The two crystalline compounds are very easily separated with the aid of cold benzene and the tetraphenylsilicane which is obtained from the benzene solution appears to be quite free from octaphenyl*cyclo*silicotetrane; the tetraphenyl compound was fully identified.

The oil from the light petroleum solution, examined qualitatively, seemed to be identical with the product from (B); that it is in fact triphenylsilicane is proved by its hydrogen value (Found: 85·5. Calc. for $SiPh_3H$: 85·4) and a silicon determination (Found: 11·2. Calc.: 10·8%). The residue from the distillation seemed to be similar to that from (B) and was not investigated further.

Since triphenylsilicyl chloride is not immediately decomposed by cold water, various attempts were made to reduce it to triphenylsilicane with some of the ordinary aqueous reducing agents, but none was successful.

The cost of some of the material used in this investigation was defrayed from a grant received from the Government Grant Committee of the Royal Society; this assistance is gratefully acknowledged.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 9th, 1929.*]

LV.—*The Effect of Intensive Drying on Certain Physical Properties of Benzene.*

By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and PERCY LUCOCK ROBINSON.

IT is now usual to discuss the experimental data of the intensive drying of liquids in terms of hypotheses postulating that a chemically *pure liquid is a system of two or more components in equilibrium*, the equilibrium in the " wet " liquid being so mobile that the system behaves as if one component only were present. That these components consist of molecules or molecular aggregates differing in size and behaving in certain circumstances as individual molecular species was originally suggested by Baker and Baker (J., 1907, **91**, 1862; 1912, **101**, 2339) and appears to be accepted by others who have propounded explanatory hypotheses (*e.g.*, Smits, *Z. physikal. Chem.*, 1922, **100**, 477; " Theory of Allotropy," 1922, p. 319; J., 1926, 2655; G. N. Lewis, *J. Amer. Chem. Soc.*, 1923, **45**, 2836; Mali, *Phil. Mag.*, 1928, **5**, 609).

The basis for this view lay in the changes, apparently far greater than any conceivable experimental error, observed in the boiling point, vapour pressure, and surface tension of liquids sealed up with phosphoric oxide in glass apparatus.

Subsequently the changes which might be brought about by intensive drying were summarised by Smits (*loc. cit.*) as the fixing of a specific proportion between the components after the normal equilibrium had either not been displaced or had been shifted in one or other of the two possible directions. Later work, mainly by the same author, has been directed towards realising these theoretical conclusions in practice, and the criteria adopted have been measurements of vapour pressure. Some three years ago, when the work here described was under contemplation, the available evidence suggested the probability that a considerable movement in the equilibrium preceded its fixation (Baker, J., 1922, **121**, 563), and the authors then felt and still feel it to be inconceivable that any considerable molecular association or dissociation could occur in a liquid without causing readily measurable changes in density as well as in surface tension. Surface-tension changes had already been observed (Baker, *loc. cit.*) in statically dried bromine, benzene, and hexane, which could be held to imply increases in the mean molecular weight of 49, 165, and 244%, respectively, but in spite of these indications of extensive association no change was found in the density of benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, or nitrogen tetroxide

after intensive drying, although the dilatometric method used should have sufficed to show changes as small as 1 part in 10,000 parts. This serious discrepancy between density and surface-tension data is still unexplained, although certain doubts have recently been thrown by Smits (J., 1928, 2399) on the validity of Baker's surface-tension measurements. The present investigation was begun with the express purpose of measuring from time to time the density and surface tension of pure benzene during the progress of its drying with phosphoric oxide. Some of the pieces of apparatus used were designed so that these measurements could be made on the liquid as a whole or on a head, middle, or tail fraction of it. The results of the first experiment led to an extension of the inquiry in two directions, *viz.*, (i) the effect of contact between the liquid and the drying agent, and (ii) the effect of the mode of preparation of phosphoric oxide. To facilitate the drying process, the volume of each piece of apparatus was kept as small as possible, the quantity of phosphoric oxide was made relatively large, and in most cases the liquid was continuously circulated by evaporation and condensation. Surface tensions were measured by the method of capillary rise, and densities by means of glass floats as previously described (Robinson and Smith, J., 1926, 1273).

EXPERIMENTAL.

Materials.—After some preliminary experiments with ether, benzene was selected as a suitable liquid, because it has less tendency to react chemically with either phosphoric oxide or metaphosphoric acid than any other material at once so accessible and so easily purified. The stock benzene used for all the experiments described below was prepared from A.R. material supplied by British Drug Houses; this was freed from thiophen by repeated treatment with sulphuric acid, washed several times with caustic soda solution and water, dried for some months over calcium chloride, and finally twice fractionally distilled from fresh calcium chloride through an 18-inch glass-spiral column.

Phosphoric oxide was prepared by redistilling good quality oxide in an apparatus * in which the distillation could take place at temperatures up to 600° in an atmosphere of either air or oxygen, and the product could be collected and sealed up in tubes 1" × 9" without coming in contact with undried air.

Preparation of Apparatus.—After being carefully tested for air leaks, each piece of glass-ware was steeped in chromic–nitric acid mixture, thoroughly washed with water, and then successively

* This apparatus was specially constructed by Mr. T. W. Parker, B.Sc., and one of us (P. L. R.), and will be described in a subsequent communication.

with alcohol and ether, and dried at 150° in an electrically heated oven. Immediately before use, the apparatus was finally dried by 7 days' heating at 400° in a large electrically heated oven of special design, while there passed through it a slow current of clean air dried by passing first through concentrated sulphuric acid in two Drechsel bottles and an inclined tube 3 feet long, and finally through a 5-foot tube packed with phosphoric oxide and glass wool.

The capillaries used for surface-tension measurements were specially drawn for us from Pyrex glass. All the capillaries were specially selected for circularity of cross section and uniformity of bore, the former by examination with a microscope, and the latter by measurement of the length of a thread of pure dry mercury in overlapping positions after the tubes had been cleaned in the manner described above. Lengths of suitable uniformity were cut from the tested sticks, and the radii determined by the two-thread method (Harkins, *J. Amer. Chem. Soc.*, 1919, **41**, 499). All lengths were measured with a travelling microscope (made by the Cambridge Scientific Instrument Co.) reading directly to 0·01 mm. and by estimation to 0·002 mm., and the weighings were made with calibrated weights and have an error not exceeding 0·02 mg. The capillary rises were measured with a special cathetometer reading to 0·02 mm. and made by the same firm. As single tubes were used in all cases, no great absolute accuracy is claimed for the surface-tension measurements, because the level of the liquid outside the capillary cannot be measured with the same accuracy as that of the liquid within it (see Mills and Robinson, J., 1927, 1823), but by taking as the outer level that part of the larger meniscus which could be very sharply focussed, comparative results consistent to within $\pm$ 0·05 dyne/cm. could be readily obtained. All *measurements were taken on a falling thread and were continued* until the required degree of constancy with time was attained.

The floats were made from Durosil tubing of suitable bore and wall thickness, and were kept as short as possible so that they could be used in small volumes of liquid. They were calibrated either in "stock" benzene before introduction to the apparatus or in the liquid to be dried immediately after sealing up. It was found that floats of this character change in density if maintained at 400° for long periods (probably owing to slight yielding of the glass under pressure), hence only those not treated in this manner could be calibrated before sealing up in the apparatus. The flotation temperatures recorded are in each case the mean of not less than eight individual readings, and are corrected for stem exposure.

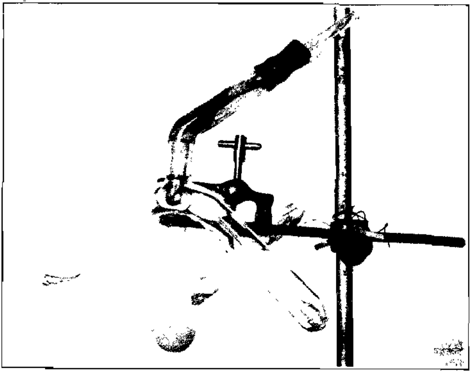


PLATE 1.

[To face p. 870.]

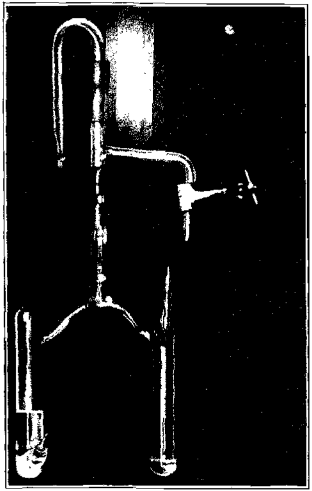


Plate II.

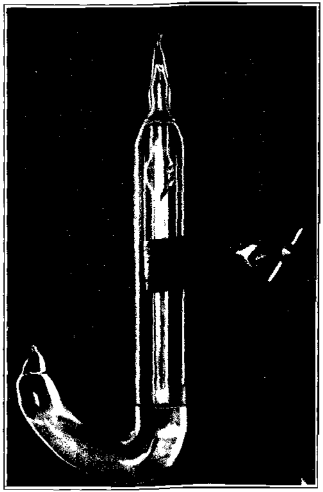
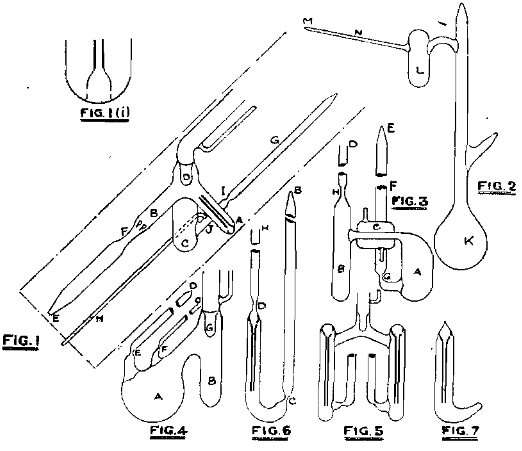


Plate III.

Experiment I.—This apparatus (Fig. 1; Plate I) was of Pyrex glass freed from capillaries by the method of Smits (J., 1926, 2658), special care being taken that the portion *A* was as cylindrical and as free from optical distortion as possible. It consisted essentially of three limbs, *A*, *B*, and *C*, meeting at the internal condenser *D* which, by a suitable inclination of the apparatus, could deliver condensate into any desired limb. To the bottom of *A* was fused the perforated conical base piece carrying the capillary, as illustrated in Fig. 1 (i), and the two floats were placed in *B*, after which *E* was



drawn down to a fine capillary. The end of *G* was closed and the apparatus placed in the heater (represented by the broken lines), leaving the ends of *H* and *E* protruding as inlet and outlet respectively for the current of dry air.

After the final heating already described, the apparatus was allowed to cool with a slightly increased air stream, and then the floats were slid into position and *E* was sealed off at *F*. Finally *G* was opened, by cracking off the taper portion, and fitted with a 3-inch extension of stiff rubber tubing of the same diameter into which was quickly thrust a tube containing distilled phosphoric oxide, the tapered end of which had been smashed the instant

previously by means of a pair of pliers. The oxide, which had been distilled in oxygen at a red heat, was shaken as a non-adherent powder down *G* into *C*, and *G* was sealed off at *I*. During this operation a positive pressure of dry air was maintained in the apparatus. Stock benzene, dried for a month over redistilled phosphoric oxide in the evacuated apparatus shown in Fig. 2, was distilled from *K* to *L*, the tip *M* was broken, and the required quantity of liquid was poured down *H* (Fig. 1) immediately after the removal of the tube delivering air. Then the benzene in *C* was gradually cooled while the apparatus was thoroughly evacuated through *H* and sealed off at *J*.

The data for the capillary tube, which was normally used between the 4- and 5-cm. positions, and the float calibrations are given in Table I, the densities of benzene found by Tyrer (J., 1914, **105**, 2540) being employed.

TABLE I.

Uniformity of Capillary.

Approx. position.	Length of thread, mm.	Approx. position.	Length of thread, mm.	Approx. position.	Length of thread, mm.
7·5	17·935	5·0	17·940	2·0	17·935
7·0	17·930	4·0	17·960	1·0	17·910
6·0	17·910	3·0	17·950	0·0 (bottom)	17·915

Mean radius of capillary : 0·215 mm.

Calibration of Floats.

	Flotation temp.	Density at flotation temp.
I	20·283°	0·878635
II	11·695	0·887927

Within a short time of filling, the whole of the benzene was distilled into *B* and the flotation temperature of each float was carefully determined. In calculating the density from the flotation temperature it was assumed that the benzene was still of normal density. Subsequently the liquid was transferred to *A* and the capillary rise of the liquid as a whole was determined. Periodically densities and surface tensions of various fractions were measured, with the results recorded in Tables II and III respectively. During most of the intervals between readings the apparatus was tilted so that the liquid refluxed from the phosphoric oxide. Generally the difference between the temperature of the laboratory and that of the water supply sufficed to maintain a steady movement of material, and when, as occasionally happened in summer, the water was too warm, evaporation was assisted by the heat from a carbon filament lamp.

TABLE II.

(t = Flotation temperature; d = density.)

Date.	Tail fraction. t.	Tail fraction. d.	Head fraction. t.	Head fraction. d.	Whole. t.	Whole. d.
July 4/27					11·695° 20·283	0·87894
6					11·684 20·278	0·87894
8			(11·684°) 20·267	0·87892	(11·684) 20·274	0·87894
11					(11·684) 20·267	0·87892
27			(11·677) 20·264	0·87892		
28	(11·627°) 20·281	0·87894				
Aug. 15			(11·677) 20·266	0·87892		
17	(11·677) 20·288	0·87895				
Oct. 30			(11·669) 20·248	0·87890		
31	(11·669) 20·265	0·87892				
Jan. 23/28					11·669 (20·260)	0·87892
May 2			(11·669) 20·248	0·87890		
3					(11·667) 20·253	0·87891
4					(20·253) 11·666	0·87891
11	(11·669) 20·256	0·87891				
14	11·664 (20·256)	0·87891				
Oct. 29					(11·664) 20·258	0·87891

N.B.—The flotation temperatures in parentheses were determined by estimation, not experimentally.

TABLE III.

(h = Capillary rise; γ = surface tension.)

Date.	Tail fraction. h.	Tail fraction. γ.	Head fraction. h.	Head fraction. γ.	Whole. h.	Whole. γ.
July 6/27					30·96	28·7
11					30·64	28·4
27			30·49	28·3		
28	30·51	28·3				
Aug. 15			30·64	28·4		
17	30·60	28·4				
Oct. 30			30·58	28·4		
31	30·40	28·2				
Jan. 23/28					30·59	28·4
April 27			30·48	28·3		
May 3					30·58	28·4
14	30·52	28·3				
Oct. 27					30·60	28·4

Experiment II.—Two cylindrical vessels, *A* and *B* (Fig. 3), were joined by a horizontal tube with a water-jacket *C*, all made of capillary-free Pyrex glass, and a float of suitable density was introduced into *B*. After the heating at 400° for 7 days, with a slow current of dry air passing in at *D* and out through the fine jet *E*, the apparatus was allowed to cool, phosphoric oxide which had been distilled in oxygen at red heat was introduced through the wide tube *F* in the same expeditious manner as described in Exp. I, and *F* was removed by sealing off at *G*. About 10 c.c. of stock benzene, not previously dried with phosphoric oxide, were poured into the apparatus through *D*. For this purpose the tube carrying air was removed and, after the liquid had been poured in, was replaced by the tube from the pump, the interval during which the tube *D* was open to air being made as small as possible. The liquid was cooled and the apparatus evacuated with the Hyvac pump and finally sealed off at *H*. The flotation temperature (*t*) of the float was accurately determined as soon as possible, and further readings were made from time to time. During some of the intervals the liquid was refluxed from the phosphoric oxide, whilst in others it stood in either *B* or *A*. As only one float was used, the results (Table IV) are not converted to densities.

TABLE IV.

Date ...	July 19, 1927.	July 27.	Aug. 17.	Jan. 23, 1928.	May 2.	Oct. 30.
t	16·556° (calibration)	16·481°	16·607°	16·606°	16·520°	16·575°

Experiment III.—In this apparatus (Fig. 4), also of capillary-free Pyrex glass, a large chamber *A* led into a narrow float vessel *B*, so that density measurements could be made on a small volume of liquid and a larger proportion of phosphoric oxide could be used. The usual heating at 400° was conducted with the air current entering at *C* and emerging at *D*. In this case, before the addition of phosphoric oxide, which had been distilled at 450—500° in oxygen, the two floats which had been previously calibrated in "stock" benzene were introduced into *D* and slid over into *B*. Afterwards, *D* was sealed off at *E*, 8 c.c. of stock benzene were introduced through *C*, the liquid was cooled, and the apparatus evacuated and sealed off at *F*. The quantity of oxide was such that when the whole of the benzene was in *A* no liquid was visible. From time to time density measurements were made on the whole of the liquid (Table V), and in the intervals the liquid was sometimes refluxed from the phosphoric oxide by means of the internal condenser *G* or allowed to stand in either *A* or *B*. The pre-sealing

calibration of the floats gave 19·957° and 14·544°, corresponding respectively to densities 0·878988 and 0·884853 at these temperatures.

TABLE V.

Date.	Flotation temps.		d.	Date.	Flotation temps.		d.
—	14·544°	19·957°	0·87894 (calibration)	Oct. 25	14·687°	20·090°	0·87909
1927.				1928.			
Oct. 17	14·605	20·057	0·87905	Jan. 26		20·102	0·87910
18	14·650	20·075	0·87907	May 2		20·106	0·87911
21	14·655	20·069	0·87906	Oct. 29		20·105	0·87911

Experiment IV.—This apparatus (Fig. 5) consisted essentially of two cylindrical vessels, with sealed-in capillary tubes cut from the same stick and of very nearly uniform diameter (0·460 mm.). The connecting tube carried an internal condenser (see Plate II) which could be used for delivering condensate into either capillary vessel. After the usual drying, the apparatus was charged with phosphoric oxide (distilled at red heat in a current of oxygen) and with 20 c.c. of benzene as already described. This benzene had been sealed up with phosphoric oxide in the vessel (Fig. 2) since part of it had been used in Experiment I. Surface-tension measurements were made with the liquid both in contact with and out of contact with phosphoric oxide (Table VI).

TABLE VI.

Date.	Liquid in contact with P_4O_{10}. h.	γ.	Liquid not in contact with P_4O_{10}. h.	γ.
(Calibration)			28·90	28·7
Feb. 3/28	29·20	29·0	29·32	29·1
24	29·20	29·0		
April 26	29·34	29·1		
May 14	29·20	29·0		
July 6	29·23	29·0		
Oct. 4	28·96	28·7		
27	29·14	28·9		

Experiment V.—This apparatus was of soft glass and had the form illustrated in Fig. 6. The air used during drying passed in at *H* and out at *B*. It was charged through *B* with phosphoric oxide (distilled at 500° in oxygen), sealed off at *C* and the stock benzene added through *H*, which after cooling and evacuation was sealed off at *D*. The quantities were arranged to give a layer of liquid into which the end of the capillary ($r = 0·213$ mm.) dipped just overlying the phosphoric oxide as illustrated in Fig. 7 (Plate III). Before surface tension readings were taken, the liquid was invariably allowed to pass twice or thrice up and down the capillary tube by tilting the apparatus so as to ensure wetting of the capillary walls. The results are given in Table VII.

TABLE VII.

Date.	h.	γ.	Date.	h.	γ.
Feb. 11/28	31·90	28·3	May 14	31·90	28·3
13	31·78	28·2	July 6	32·02	28·5
April 25	32·12	28·5	Oct. 4	31·94	28·3
May 1	32·02	28·5	27	32·10	28·5
2	32·01	28·5			

Experiment VI.—The apparatus, of soft glass, was identical with that used in Expt. V, but in this case it was not dried at 400° and the phosphoric oxide used was commercial oxide, free from lower oxides but not distilled, the method of charging being by dropping plugs of the oxide, compressed in a glass tube, into the apparatus without the use of a counter-current of dry air. Stock benzene was used, and the radius of the capillary was 0·206 mm. Results are given in Table VIII.

TABLE VIII.

Date.	h.	γ.	Date.	h.	γ.
Feb. 14/28	31·34	28·7	July 6	31·41	28·7
April 25	31·24	28·6	Oct. 4	31·38	28·7
May 2	31·42	28·7	27	31·53	28·7
14	31·44	28·7			

Discussion of Results.

The mean densities of the head and tail fractions of the benzene in Expt. I, comprising in each case about one-third of the volume of the liquid, are 0·87892 and 0·87893 respectively, whilst that of the whole material is 0·87893. During the 16 months of contact with phosphoric oxide, these portions show a fall in density of 0·00002, 0·00003, and 0·00003, respectively. The capillary rises for head and tail portions show only very slight changes in surface tension over the period, but for the liquid as a whole a fall of 0·30 unit is observed, occurring almost entirely in the first few days. The flotation temperatures obtained in Expt. II may indicate density changes of the order of 0·00007, but nevertheless show that these changes are but temporary, the liquid regaining its original density. Expt. III indicates that an increase in density of the order of 0·0001 may take place in ordinarily dry benzene immediately after it has been brought into contact with phosphoric oxide. Subsequently a steady increase amounting to 0·00005 over the total period of drying is recorded, which is comparatively small and is, strangely enough, opposite in sense to the corresponding change in Expt. I. Expt. IV was set up to test whether the surface tension of benzene was affected by contact with a surface of phosphoric oxide in the manner described by Baker (J., 1927, 949) for other catalysts, whilst Expt. VI carried on the same inquiry in a rather similar manner in an apparatus of soft glass with benzene which had not been sub-

jected to a treatment with phosphoric oxide. Neither these nor Expt. V, which differed somewhat from them, gave indication of significant change in surface tension at the date of the last observation (Oct. 1928).

The changes in density now recorded do not exceed about 5—7 parts in 100,000 parts, and thus support Baker's previous conclusion (*loc. cit.*) that intensively dried benzene does not change in density by 1 part in 10,000 parts. This conclusion has now been extended, however, to include not only the liquid as a whole, but also the various fractions obtainable from it by distillation. When first brought into contact with phosphoric oxide, benzene increases in density by about 1 part in 8,000 parts: the view that this is due to dissolution of the oxide is supported by the observation that the evaporation of benzene in contact with phosphoric oxide invariably left white striæ of residue which could be removed by repeated washing with distilled benzene.

The unexpected discordance between the present surface-tension measurements and those previously recorded by Baker is disconcerting and difficult to explain. In 16 months, under conditions designed in every way to facilitate drying, the maximum observed change in capillary rise is 0·4 mm., and that in the direction of a *decrease* in surface tension, whereas the *increase* in surface tension recorded by Baker after a year's drying would have given, even in these wider capillaries, an increased capillary rise of about 6 mm. Though material changes may yet occur, the conclusion at this stage is, evidently, that intensive drying has not produced any change in the density or surface tension of benzene such as would justify an assumption of appreciable change in degree of association or of fractional separation of pseudo-components. It may be said that the duration of these experiments is insufficient, but there are numerous cases cited in the literature where effects attributed to intensive drying have been observed in shorter periods, and, though our experiments cannot yet suffice to prove a negative, it seems useful to record at this stage the evidence they have so far afforded. The experiments will be continued and may yield results of interest some years hence.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research, enabling one of us (J. B. P.) to take part in this work, and to the Research Fund Committee of this College for a grant towards the cost of the cathetometer used throughout this investigation.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, October 31st*, 1928.]

LVI.—*The Mechanism of Thermal Decomposition of the Normal Paraffins.*

By Ernest Noel Hague and Richard Vernon Wheeler.

Since Berthelot (*Compt. rend.*, 1866, **62**, 905) put forward his well-known theory regarding the mode of decomposition of hydrocarbons by heat, in which acetylene played the most important part as an early product of degradation and as " générateur fondamental des carbures pyrogenés," the literature relating to the subject has become extensive, and several attempts have been made to evolve a theory which will embrace all the observed facts, which Berthelot's does not.

Of the more important observations must be mentioned those of Thorpe and Young (*Proc. Roy. Soc.*, 1871, **19**, 370), Haber (*Ber.*, 1896, **29**, 2691), Bone and Coward (J., 1908, **93**, 1197), Davidson (*J. Ind. Eng. Chem.*, 1918, **10**, 901), and Calingaert (*J. Amer. Chem. Soc.*, 1923, **45**, 130).

Thorpe and Young distilled solid paraffins under pressure, obtaining mixtures of liquid paraffins and olefins which led them to suggest a general reaction involving a simultaneous formation of hydrides and olefins; according to this, the primary decomposition of butane would be $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_3 + CH_2{:}CH_2$.

Haber examined *n*-hexane, in particular, and found that between 600° and 800° the primary decomposition involved the elimination of methane, leaving one of the next lower olefins, C_5H_{10}.

Bone and Coward, from the action of heat on methane, ethane, ethylene, and acetylene, concluded that methane was the most stable and was always a principal product of decomposition of the others, particularly above 800°, when one of the main reactions was the hydrogenation of such residues as $\vdots CH$, $:CH_2$, and $\cdot CH_3$ (which might have momentary separate existence).

Davidson, continuing work by Zanetti (*J. Ind. Eng. Chem.*, 1916, **8**, 674, 777), studied the " cracking " of the ethane–propane fraction of natural gas, paying particular attention to the formation of aromatic hydrocarbons, which were accompanied by olefins and diolefins. Acetylene was absent, though the temperature used was insufficient to decompose it had it been formed. Arguing on the results of experiments by Jones (J., 1915, **107**, 1582), Davidson concluded that the aromatic hydrocarbons were produced by condensation of the olefins, with elimination of hydrogen.

Calingaert attempted to determine the initial stage in the decomposition of *n*- and *iso*-pentane, limiting the temperature to 600°. The results suggested that with *n*-pentane for the most part th

carbon chain was ruptured in such a manner as to give an ethyl and a propyl group, one of which was then saturated at the expense of the other, yielding either (*a*) ethane and propylene or (*b*) ethylene and propane. To a certain extent, methyl and butyl groups could be formed, yielding methane and butylene.

From our own study of the action of heat on the unbranched-chain paraffins, from ethane to *n*-hexane, we conclude that the primary decompositions can be represented by series of equations indicating the rupture of the chain at any position, with the production of an olefin and the complementary lower paraffin or, at the limit, hydrogen. Thus with ethane, propane, and *n*-butane we have found the primary decompositions to be :

Ethane : (i) $CH_3{\cdot}CH_3 = CH_2{:}CH_2 + H{\cdot}H$.

Propane : (i) $CH_3{\cdot}CH_2{\cdot}CH_3 = CH_2{:}CH_2 + CH_3{\cdot}H$,

(ii) $CH_3{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + H{\cdot}H$.

n-*Butane :* (i) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_2{:}CH_2 + CH_3{\cdot}CH_2{\cdot}H$,

(ii) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + CH_3{\cdot}H$,

(iii) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + H{\cdot}H$.

With each hydrocarbon, the reactions are given in order of their importance. As the series is ascended, the tendency for hydrogen to be eliminated, leaving an olefin with the same number of carbon atoms as the original paraffin, rapidly diminishes.

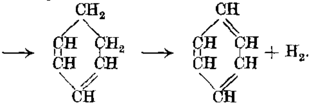
Equations (i) and (ii) for propane have recently been suggested, as conforming with the results of their experiments, by Pease (*J. Amer. Chem. Soc.*, 1928, **50**, 1779) and Frey and Smith (*J. Ind. Eng. Chem.*, 1928, **20**, 948), who have also suggested equation (i) for ethane. Of the four possible equations for *n*-pentane, Calingaert (*loc. cit.*) noted the first three.

Following these primary decompositions, many complicated reactions occur during "pyrosynthesis" at the same or higher temperatures. With ethane, for example, at temperatures above 700°, the hydrogenation of fugitive "residues," $:CH_2$, as suggested by Bone and Coward (*loc. cit.*), would seem to occur. At comparatively low temperatures, subsequent to the formation of ethylene, butadiene is produced from each of the paraffins (compare Norton and Andrews, *J. Amer. Chem. Soc.*, 1886, **8**, 1). Above the range 700—750°, under the conditions of our experiments, benzene and other aromatic hydrocarbons are produced from each gas (methane included). At this stage of the syntheses, ethylene appears to be the starting point. Our experiments show that ethylene readily polymerises to butylene which, by elimination of hydrogen, yields butadiene. From the presence of six-membered unsaturated hydrocarbons (liquids, b. p. 59° and 78°) amongst the synthetic products

from the paraffins, we conclude that the butadiene reacts with ethylene (compare Jones, *loc. cit.*), the suggested mechanism being :

(*a*) $CH_2\colon CH_2 + CH_2\colon CH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH\colon CH_2 \longrightarrow$
$CH_2\colon CH{\cdot}CH\colon CH_2 + H_2$.

(*b*) $CH_2\colon CH{\cdot}CH\colon CH_2 + CH_2\colon CH_2 \longrightarrow$ *either*
$CH_2\colon CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH\colon CH_2$ *or* $CH_2\colon CH{\cdot}CH\colon CH{\cdot}CH\colon CH_2 + H_2$



Further, by analogy with the formation of diphenyl from benzene it is reasonable to suppose that butadiene can condense with benzene hydrogen being eliminated, to form naphthalene ; and that anthra cene and phenanthrene can be formed from the naphthalene in ‹ similar manner.

The first member of the series, methane, requires separate con sideration. Although the absence of a C—C linkage causes it behaviour to be different from that of the higher members, it decomposition point being about 200° higher than that of ethane whereas there is but a 25° interval between the decompositio points of the others, yet liquid hydrocarbons in quantity ar produced from methane, the formation of benzene being at it optimum over the range 1000—1100°.* As Bone and Cowar (*loc. cit.*) have shown, the main decomposition of methane is ult mately to carbon and hydrogen. At comparatively low tempe atures, however, ethylene is formed. As with other paraffins, w regard this ethylene as the source, through butadiene, of the benzer and other aromatic hydrocarbons produced. The mechanism ‹ the early decomposition may be expressed by $CH_3{\cdot}H \longrightarrow \colon CH_2 + H{\cdot}$I two of the CH_2 residues, of fugitive existence as postulated by Bo and Coward, combining to form ethylene.

With regard to our suggested mechanism of the primary decon positions of the paraffins possessing a carbon chain, Professor T. I Lowry has pointed out to us an analogy with the mechanism reversible *isomeric changes which he has been good enough outline in an addendum to this paper.*

* In the publication of these observations we have been anticipated Fischer (*Brenn. Chem.*, 1928, 9, 309), whose method of experiment has be almost identical with our own. We confirm his results in all imports particulars.

EXPERIMENTAL.

The Hydrocarbons.—Methane was obtained from a blower of firedamp at a coal-mine in South Wales. The firedamp contained no other inflammable gas, but some nitrogen and carbon dioxide were present. The methane was purified by liquefaction. Our main supplies of ethane, propane, and *n*-butane were obtained compressed from America, where they had been fractionated from natural gas. They were already of a high degree of purity, but in each instance they were liquefied and fractionated before use. Check experiments were made with propane and *n*-butane prepared by the Grignard reaction, liquefied, and fractionated. The purity of the gases was tested by their boiling points and by explosion analyses. The liquid hydrocarbons, *n*-pentane and *n*-hexane, were obtained from as pure a source of supply as possible and fractionated many times to ensure that only the unbranched-chain paraffin was present. The purity of the final products (the yields of which were often poor) was checked by density determinations.

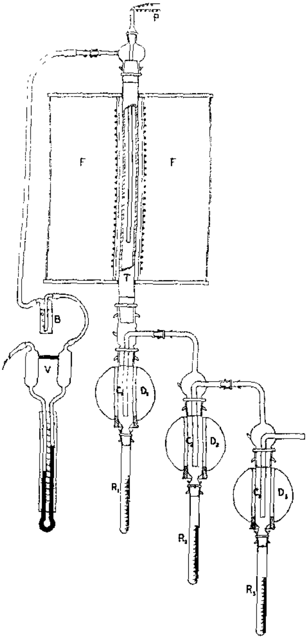
Method of Experiment.—With each hydrocarbon three types of experiment were made: (1) *static*; (2) *circulation*; and (3) *stream*, in which large volumes of each gas were passed at a constant rate through a tube of quartz heated at a constant temperature, the liquid and gaseous products of decomposition being collected. Only the "stream" experiments need be described.

Stream Experiments.—The apparatus used is shown diagrammatically in Fig. 1. The gas was passed through a Venturi meter, V, and a bubbler, B, to the upper end of the reaction tube, T, which was supported vertically within an electric furnace, F. The reaction tube was 70 cm. long and of 2·2 cm. internal diameter. A narrow quartz tube, P, with its lower end closed so as to form a pocket for a thermocouple, was arranged axially within the reaction tube. On issuing from the reaction tube, the gases passed through three condensers, C, in series, cooled by solid carbon dioxide dissolved in ether, contained in Dewar vessels, D. Attached to the bottom of each condenser were graduated receivers, R. Ground joints were used throughout the apparatus.

In carrying out an experiment, a stream of nitrogen was passed through the apparatus until all air had been swept out. Connexion was then made to the supply of hydrocarbon, the rate of flow of which was adjusted to 4 litres per hour. In each experiment, from 12 to 16 litres of gas were passed. The resultant gases, after passing through the condensers, were either bubbled through bromine water or, at the end of the first hour, collected in a gas holder for analysis, their volume being measured. At the conclusion of an experiment, the stream of hydrocarbon was replaced by one of

nitrogen, and the furnace allowed to cool. The condensers were disconnected, stoppered, and gently warmed so as to allow their frozen contents to melt and flow into the graduated receivers, which were then removed and stoppered.

Fig. 1.



The liquid products of decomposition were weighed and distilled over different temperature ranges. In recording the results, the fraction boiling at a low temperature (mainly between 80—90°) is referred to as the "benz-ene fraction." It con tained 85—95% of benz ene, with, at the lowe temperatures of decom position, some unsaturatec hydrocarbons. The gase ous products were analysec and in some experiment liquefied, with subsequen fractionation. In othe experiments they wer brominated. Record were kept of the amoun and character of the ca bon deposited within th reaction tube, which wa thoroughly cleaned b burning out between su cessive experiments.

When a liquid paraffi was used, the procedu was modified slightly, th liquid being run directl into the reaction tube b allowing it to trickle down the thermocouple sheath, the rate flow (0·166 g.-mol. per hour) being comparable with the rate of litres per hour used for the gases.

Gas Analysis.—Owing to the complexity of the mixtures obtain at temperatures below 750°, accurate gas analyses often could not made. The higher paraffins, propane in particular, are soluble

some of the reagents used for estimating other constituents, whilst ethylene, when present in high concentration, is appreciably soluble in the ammoniacal silver chloride used for estimating acetylene. When comparing the analyses, the fact that some ethylene is recorded as "acetylene" should be borne in mind. In some of the experiments at the lower temperatures the gases were brominated, the bromides fractionated under reduced pressure, and the unsaturated hydrocarbons regenerated by means of a zinc–copper couple, according to the scheme suggested by Manning, King, and Sinnatt (Fuel Research Board, Tech. Paper No. 19, 1928). The products of decomposition above 750° did not present any difficulty, since the unsaturated hydrocarbons were much diluted with methane and hydrogen and the higher paraffins had been mostly decomposed.

Results of Experiments.—The results obtained from the "stream" experiments with each hydrocarbon are summarised in the tables that follow, the percentages of total liquids, "benzene" fraction, and carbon being given by weight, and others by volume.

TABLE I.

The Decomposition of Methane.

Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_4.	H_2.	CH_4.
900°	—	1·2	—	—	0·6	2·8	14·0	82·6
950	3·7	2·0	1·1	Trace	0·9	3·7	31·5	63·9
1000	16·6	3·7	3·2	1·4	0·4	2·8	42·6	54·2
1050	27·5	2·6	1·7	4·5	0·3	2·1	54·3	43·3

Methane (see Table I). At 1000°, crystals of naphthalene were formed. The gaseous products of decomposition at 950° were brominated. Distillation of the bromides showed the presence of ethylene dibromide and butadiene tetrabromide. The liquids distilling below 170° for the most part (about 95%) boiled at 80° and were found to be benzene. A small quantity boiled between 76—80°. The liquids of high boiling point contained naphthalene and anthracene.

Ethane (see Table II). There were no liquid products at 700°,

TABLE II.

The Decomposition of Ethane.

Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.	C_2H_6.
700°	32·7	Nil	Nil	Nil	1·7	2·8	21·3	21·9	2·7	49·6
750	63·0	2·1	—	Trace	4·7	4·3	24·3	32·3	13·3	21·1
800	63·9	9·7	6·9	—	3·7	3·0	21·1	38·4	21·1	12·7
850	—	17·9	11·2	—	1·7	2·3	14·7	41·4	32·4	7·5
900	71·0	21·9	10·6	8·1	1·6	1·8	5·0	44·3	38·9	8·4
950	87·5	12·8	8·0	13·9	0·4	1·0	3·8	52·6	40·8	1·4
1000	100·0	5·5	3·6	16·2	0·3	0·8	2·4	58·5	33·9	4·1

whereas Williams-Gardner (*Fuel*, 1925, **4**, 430), working in these laboratories, obtained traces when using a much slower gas-stream ($\frac{1}{2}$ l. per hour). At 750°, a high proportion of the liquids obtained was found to be unsaturated. The gases were liquefied (by liquid air) and brominated, the white crystalline solid, m. p. 114°, obtained being proved to be butadiene tetrabromide. At 800°, crystals of naphthalene were deposited, and the gases contained butadiene. At 850°, the gases contained a small quantity of butadiene, whilst the liquids distilled mainly between 80—85°, and proved to be benzene. At 900°, the liquids contained much heavy oil, only about half distilling between 80—100°. At 950°, much naphthalene was formed, and more than half the liquid condensed was benzene.

As the temperature of decomposition was raised from 750°, the total yield of liquid products increased until a maximum was reached at 900°, the yield then representing 21·9% by weight of the ethane passed. The fraction of the liquids boiling between 80—90° was at a maximum for the decomposition at 850°. The liquids formed at 750° were chiefly unsaturated hydrocarbons, but the low-boiling fraction obtained at 850° and above was nearly pure benzene, the residual oil being composed chiefly of naphthalene and anthracene.

From the gas analyses and the volume changes, it will be seen that at 700° about 90% of the ethane that decomposed did so according to the equation $C_2H_6 = C_2H_4 + H_2$. As the temperature of decomposition was raised, the proportion of hydrogen formed continuously increased, whilst that of the ethylene reached a maximum and then rapidly decreased. Methane and the higher olefins, it would seem, are secondary products of decomposition, for the proportion of methane increased with rise of temperature to 950°, thereafter decreasing, and that of the higher olefins reached a maximum at 750°. Butadiene was found in the gases at 750°, 800°, and 850°.

It will be noticed that at no temperature did the ratio CH_4/H_2 in the products of decomposition in these "stream" experiments reach the high value 1·94 found by Bone and Coward (*loc. cit.*) on heating ethane in closed tubes, a result which, with other considerations, led them to postulate the transitory existence of unsaturated $:CH_2$ residues. We confirm the high value of this ratio when ethane is heated in closed tubes at 800° during $\frac{1}{2}$ hour, and conclude therefrom that the formation of methane by the hydrogenation of $:CH_2$ residues (arising from the partition of the ethylene molecule) is a secondary reaction.

Propane (see Table III). The percentages of methane are minimum values, calculated from explosion analyses, after all but paraffins had been absorbed, on the assumption that only methane

TABLE III.

The Decomposition of Propane.

Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
700°	52·5	1·0	—	—	14·2	3·4	19·7	11·8	14·1
750	88·8	6·9	4·2	—	13·3	7·1	20·5	13·3	26·8
800	105·0	17·0	10·1	Trace	3·4	2·9	19·7	20·8	38·8
850	106·2	23·1	11·6	0·9	2·3	2·5	14·5	26·6	46·2
900	119·0	20·1	9·7	5·0	1·4	1·8	9·8	33·4	45·8
950	144·0	10·3	5·4	11·3	0·5	1·1	6·1	44·0	41·5
1000	159·0	5·5	2·2	18·3	0·5	1·1	5·8	51·3	36·1

* Minimum values.

and ethane (not recorded in Table III) were present. Actually, there was some undecomposed propane at the lower temperatures. A direct (rough) estimation of propane in the mixed paraffins from the decomposition at 700°, by absorption with absolute alcohol, showed them to contain about 30%. The figure for methane in that analysis should therefore be raised to about 20%.

At 750°, a mobile liquid was obtained, *d* 0·635, fractions of which boiled at 80°, 91°, and 102°. At 850°, a high proportion of the liquids boiled between 80—90°, and a further portion at 108°. Butadiene was found in the gases at 750°, 800°, and 850°.

The yield of liquid products reached a maximum at 850°, representing 23·0% of the propane passed. The liquids obtained at temperatures below 800° did not solidify in the cooled receivers (about −80°) and were mainly unsaturated hydrocarbons. Above 800°, they were mainly aromatic.

A study of the gas analyses and volume changes shows that (1) the proportion of hydrogen increased continuously with rise of temperature of decomposition; (2) the proportion of methane reached a maximum at 850° and that of ethylene at 750°. In the products of decomposition at 700°, the proportions of ethylene and methane (corrected value) were nearly equal, indicating that the propane had decomposed in two ways: (*a*) $C_3H_8 = CH_4 + C_2H_4$ and (*b*) $C_3H_8 = H_2 + C_3H_6$, the values showing that, of the propane that decomposed, 60% did so according to (*a*) and 35—39% according to (*b*). This calculation was confirmed by estimating the propylene in the gases by the method of Manning, King, and Sinnatt (*loc. cit.*).

n-*Butane* (see Table IV). At 650°, traces of a low-boiling (−5°) oil were obtained, and bromination of the liquefied gases showed the presence of butadiene. The gases also contained a high proportion of ethane. At 700°, as with propane at 750°, an unsaturated oil, liquid at −80°, was produced. Fractions of this oil boiled at 33°

TABLE IV.

The Decomposition of n-Butane.

Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
650°	7·1	—	—	—	24·6	1·4	16·2	8·1	Nil
700	87·5	5·8	2·2	—	19·7	2·4	20·4	10·3	19·9
750	103·6	13·6	8·9	Trace	11·9	3·3	23·6	10·6	40·0
800	140·0	21·1	12·9	,,	3·6	0·7	19·0	28·2	46·2
850	—	24·5	12·7	0·9	2·1	—	15·9	25·2	51·8
900	—	20·9	9·3	6·7	0·7	—	7·9	35·0	54·2
950	215·0	8·7	4·6	19·6	0·2	—	2·0	68·1	29·7

* Minimum values.

and 93°, the bulk distilling below 70°. The gases contained butadiene and much ethane. At 750°, the bulk of the liquids boiled between 80—120°, and the gases contained butadiene and some ethane. At 800°, most of the oils solidified in the cooled condensers; the gases contained butadiene. At 850°, 900°, and 950°, the oils (chiefly benzene) became progressively darker in colour and naphthalene was formed.

The total yield of oils reached a maximum at 850°, corresponding to 24·6% of the butane passed. Most of the oils obtained at 700°, and a high proportion of those at 750°, were unsaturated hydrocarbons, but at higher temperatures benzene was the chief liquid product.

The results indicate that at low temperatures (650—700°) butane decomposes in three ways: (*a*) $C_4H_{10} = C_2H_6 + C_2H_4$, (*b*) $C_4H_{10} = CH_4 + C_3H_6$, and (*c*) $C_4H_{10} = H_2 + C_4H_8$; but the gas analyses give no clear indication as to the proportion in which the butane decomposes according to these three equations, for the proportions of propylene and butylene in the higher olefins are not disclosed by them, whilst the proportions of methane, ethane, and butane in the mixture of paraffins obtained at the lower temperature of decomposition could not be determined by explosion analysis. This information was, however, obtained in another way. The gaseous products of decomposition at 650° were passed through bromine water, and when the resulting bromides (98 g.) were distilled under reduced pressure (16 mm.), 88 g. boiling below 80° were obtained, the solid residue being chiefly butadiene tetrabromide. Part of the liquid fraction was treated with zinc–copper couple in alcohol and the olefins thus regenerated, when analysed by the method of Manning, King, and Sinnatt, showed: Ethylene, 43; propylene, 36; and butylene, 21%. Hence, about 40% of the butane that decomposed did so according to reaction (*a*), 35% according to (*b*), and 20% according to (*c*).

TABLE V.

The Decomposition of n-*Pentane.*

Temp.	Total liquids, %.	Benzene fraction, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
600°	79·2	—	15·6	4·9	17·4	6·2	24·0
700	20·0	9·7	18·1	3·3	22·8	10·6	26·4
750	16·2	7·5	8·0	2·8	24·0	13·0	41·0
800	21·4	11·6	2·9	2·1	22·2	17·2	48·5
850	26·8	11·9	1·4	1·7	17·6	29·0	45·2

* Minimum values.

n-*Pentane* (see Table V). Most of the liquid obtained at 700° boiled between 35·8—36·2° (undecomposed pentane), but a fraction distilled at 58° and was unsaturated. At 750°, decomposition of the pentane appeared to be complete, most of the oils (which solidified in the cooled condensers) distilling between 80—84°. At 800° and 850°, also, the liquid distillates were mainly benzene.

A change in the character of the products of decomposition took place at 750°, liquid aromatic hydrocarbons being then formed in increasing quantity up to 850°. The chief constituent of the gases at all temperatures was methane. The proportion of ethylene reached a maximum at 750° and that of the higher olefins at 700°. The proportion of hydrogen increased continuously with increase of temperature.

TABLE VI.

The Decomposition of n-*Hexane.*

<table>
<tr><th rowspan="2">Temp.</th><th rowspan="2">Total liquids, %.</th><th rowspan="2">Benzene fraction, %.</th><th colspan="5">Gas analyses, % (by vol.).</th></tr>
<tr><th>Higher olefins.</th><th>C₂H₂.</th><th>C₂H₄.</th><th>H₂.</th><th>CH₄.*</th></tr>
<tr><td>600°</td><td>87·7</td><td>—</td><td>23·5</td><td colspan="2">24·4</td><td>6·6</td><td>30·1</td></tr>
<tr><td>650</td><td>63·3</td><td>—</td><td>23·1</td><td colspan="2">27·6</td><td>6·6</td><td>32·9</td></tr>
<tr><td>700</td><td>35·6</td><td>—</td><td>21·8</td><td colspan="2">33·2</td><td>7·5</td><td>37·2</td></tr>
<tr><td>725</td><td>27·3</td><td>20·4</td><td></td><td colspan="2"></td><td></td><td></td></tr>
<tr><td>750</td><td>30·6</td><td>19·7</td><td>5·8</td><td colspan="2">28·4</td><td>16·1</td><td>45·3</td></tr>
<tr><td>800</td><td>33·7</td><td>19·2</td><td>3·3</td><td colspan="2">24·9</td><td>19·4</td><td>48·5</td></tr>
<tr><td>850</td><td>33·8</td><td>19·0</td><td>1·3</td><td>1·8</td><td>14·2</td><td>27·6</td><td>6·4</td></tr>
<tr><td>900</td><td>30·1</td><td>14·6</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>950</td><td>10·0</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

* Minimum values.

n-*Hexane* (see Table VI). Little of the hexane was decomposed at 600°. The gases contained butadiene. At 650° and 700°, some of the liquid collected was unsaturated, and the gases contained propylene and butylene as well as butadiene. At 750°, the oils obtained were of dark colour and solidified in the cooled condensers, boiling for the most part at 80°.

The results were similar to those obtained with n-pentane. De-

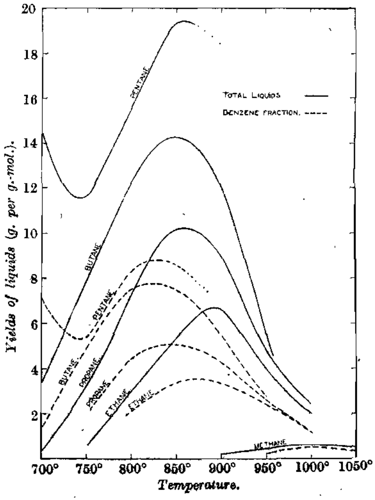
composition was appreciable at 600° and apparently complete at 725°. Above that temperature, the yield of liquids increased to a maximum at about 850°, 33·8% by weight of the hexane passed being transformed into liquid hydrocarbons (chiefly aromatic) at that temperature. The nature of the gases changed between 700—750°, corresponding with the production of aromatic hydrocarbons. At 600°, a liquid of b. p. 59° was obtained which, as judged from its similarity with liquid fractions obtained during the decomposition of butane and pentane, was 1 : 5-hexadiene. At 650°, the liquids obtained began to boil at 30°, suggesting the presence of C_5 compounds such as the amylene found by Haber (*loc. cit.*) From the gas analyses it would appear that at temperatures up to 700° the important reactions are those of "demethanation" (compare Haber), "de-ethylenation," and "dehydrogenation," in the order named.

Perhaps the most striking feature of the results considered as a whole is the similarity in behaviour of all the hydrocarbons, methane included, at the higher temperatures. Below 750°, when the primary decompositions are taking place, each hydrocarbon follows its own proper course, but at the higher temperatures the (secondary) reactions are similar with all.

The temperature range 700—750° is a transition period. Within that range, with all the paraffins except methane, the production of ethylene reaches a maximum. Under similar conditions, the same types of liquids (aromatic hydrocarbons) are obtained throughout the series from ethane to hexane. The common source of these liquids would therefore seem to be a C_2 unsaturated hydrocarbon. Acetylene has for long been regarded as the source of benzene during decompositions of this character, but recent work, *e.g.*, Davidson's (*loc. cit.*), has stressed the absence of acetylene from the gaseous products. Davidson found, also, that on passing mixtures of acetylene, ethane, and propane through a tube heated at temperatures ranging from 550—950°, acetylene could always be detected in the products even though its original concentration was as low as 0·1%. In the present work, although acetylene has been recorded in the gas analyses, treatment of the gaseous products on a large scale with ammoniacal silver chloride has yielded but traces of precipitate, whilst no acetylene tetrabromide has been obtained on their bromination. Further, on treating acetylene in a similar manner to the paraffins (see later), we have found that the maximum yields of benzene by polymerisation are obtained over the range 650—700°. Aromatic hydrocarbons would be expected from the paraffins over this temperature range were acetylene their source, whereas they are not produced below 750°.

Ethylene alone fulfils all requirements as a producer of benzene in these experiments. It is fairly stable up to 750° and yields aromatic hydrocarbons above 700°. In the decompositions of the paraffins, the yields of ethylene are proportional to the percentage yields (at a higher temperature) of aromatic hydrocarbons. Thus with ethane, propane, butane, and pentane the maximum percentage of ethylene in the products of decomposition is about 24, and the maximum yield of liquid products, expressed as a percentage by weight of the

FIG. 2.



hydrocarbon passed, is about 24 with each. With hexane, the maximum percentage of ethylene is 33·2 and the maximum yield of liquid products is 33·8%.

The yields of liquids, and the temperature ranges over which those yields were obtained, are shown graphically in Fig. 2, where the yields, expressed in g. per g.-mol., are plotted against temperatures of decomposition. The results for hexane have been omitted to avoid rendering the diagram cumbersome. As the series is ascended from ethane to pentane, the yields of liquids increase approximately

in the ratio 2 : 3 : 4 : 5, showing that the percentages (by weight) of these paraffins thus transformed are about the same. That this should be so can perhaps be deduced from the fact that the composition of the gases produced over the critical temperature-range for the formation of liquids (750—800°) is nearly the same for each of these hydrocarbons. Hexane, which yields an abnormally high proportion of ethylene, yields also abnormally high quantities of liquids.

Comparative experiments were made with ethylene and acetylene, more particularly to determine their temperatures of decomposition and polymerisation and the character of the liquid products yielded by them.

TABLE VII.

The Decomposition of Ethylene.

Temp.	Total liquids, %.	Benzene fraction, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
700°	13·5	6·6	9·2	8·2	55·2	5·9	8·7
750	25·5	13·1	4·4	4·8	40·5	13·1	28·8
800	28·9	10·7	1·4	4·2	16·1	27·9	44·0
850	15·5	7·8	0·4	1·1	6·6	35·6	50·0

* Minimum values.

Ethylene (see Table VII). Of the liquids obtained at 700° and 750° (*d* 0·8), half distilled between 80—86°, a small fraction boiling at 72—76°. The gases contained butylene and butadiene. The liquids obtained at 800° were brown; most distilled between 80—84° and some at 120—130°, leaving a residue of naphthalene.

The optimum temperature for the production of liquids (mainly benzene) was between 750—800°, the total yield at 800° representing 28·9% of the ethylene passed. The dilution of ethylene with hydrogen in certain other stream experiments resulted in decreased yields of benzene and the temperature range for the maximum yield was increased, the mixture giving results similar to those obtained with ethane. This result is consistent with the suggested primary decomposition of ethane. The gas analyses show that ethylene is fairly stable up to 750°, as appears also from the experiments with the paraffins, where the maximum concentrations of ethylene in the products of decomposition were obtained between 700—750°. The figures for acetylene in the gas analyses (Table VII) are too high for the reason previously stated. On passing the gases from decomposition at 750° and 800° through ammoniacal silver chloride, as they issued from the apparatus, only traces of precipitate were formed.

Several stream experiments were carried out at 600°, 650°, and

675°, and the resultant gases brominated. The bromides were distilled and the residual solid, after recrystallisation from alcohol, proved to be butadiene tetrabromide.

A series of experiments, for which we are indebted to Mr. W. L. Wood, M.Sc.Tech., were made in which samples of ethylene were heated at different temperatures in quartz bulbs during three hours, and the resultant gases analysed. Between 400—700° the ethylene was found to polymerise, yielding butylene, the optimum temperature being 500°. Some of the results are recorded in Table VIII.

TABLE VIII.

The Polymerisation of Ethylene.

	Gas analyses, % (by vol.).				
Temp.	Higher olefins.	C_2H_4.	H_2.	CH_4.	C_2H_6.
400°	3·5	96·5	—	—	—
450	8·0	92·0	—	—	—
500	13·7	76·0	—	—	10·3
550	7·9	55·1	2·9	12·0	22·1
600	6·0	30·0	2·7	25·4	35·1
650	4·2	19·0	11·2	52·7	12·9
700	1·9	16·5	15·4	57·5	8·7
750	0·7	8·2	18·7	67·0	5·4

TABLE IX.

The Polymerisation and Decomposition of Acetylene.

				Gas analyses, % (by vol.).				
Temp.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
600°	30·8	—	—	0·8	53·2	4·2	27·9	8·3
650	61·1	26·4	9·7	1·2	29·5	6·9	34·0	23·0
700	61·1	24·8	16·7	1·2	2·4	10·4	43·8	37·1
750	46·7	18·3	22·1	0·2	0·7	8·8	50·1	37·5

* Minimum values.

Acetylene (see Table IX). At 600°, considerable quantities of soft carbon were produced in the reaction tube and fell from it. This carbon had absorbed the bulk of the oils formed. At other temperatures much soft carbon was formed. The maximum yields of liquids were obtained over the range 650—700°, the amount representing 61·1% of the acetylene passed.

This work has been carried out for the Anglo-Persian Oil Company, to whom our thanks are due for permission to publish the results. We wish also to thank Mr. W. L. Wood, M.Sc.Tech., for assistance in the experiments.

DEPARTMENT OF FUEL TECHNOLOGY,
SHEFFIELD UNIVERSITY.
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ADDENDUM.

By THOMAS MARTIN LOWRY.

According to the mechanism of decomposition outlined in this paper, the degradation of the paraffins proceeds by the reversible elimination of a molecule HX, which may be either a paraffin of smaller molecular weight or hydrogen itself. The residue from this initial decomposition is then an olefin, and the process may be compared with the elimination of an acid or of water from any other addition compound of an olefin. Thus the decompositions represented by the equations

$$CH_3{\cdot}CH_2{\cdot}OH \rightleftharpoons CH_2{:}CH_2 + H{\cdot}OH$$

and $$CH_3{\cdot}CH_2{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons CH_2{:}CH_2 + HO{\cdot}SO_2{\cdot}OH$$

may be compared with the pyrogenic decompositions described in the present paper. A more detailed analogy can be found in Butlerow's study (*Annalen*, 1877, **189**, 44) of the equilibrium between *tert.*-amyl alcohol and *iso*amylene in presence of 50% sulphuric acid, $C_5H_{12}O \rightleftharpoons C_5H_{10} + H_2O$. The decomposition of the paraffins is thus pictured as conforming to self-established precedents, and depending on a mechanism of a very general character.

The pyrogenic synthesis is then imagined as proceeding according to two well-established processes, depending on polymerisation and on elimination of hydrogen, successively. The first of these processes, which converts ethylene into butylene, can be compared with Butlerow's conversion of *iso*butylene into *iso*dibutylene :

$$2\,{}^{CH_3}_{CH_3}{>}C{:}CH_2 \longrightarrow {}^{CH_3}_{CH_3}{>}C{:}CH{\cdot}C(CH_3)_3$$

(*Annalen*, 1877, **189**, 65). This process is merely a reversal of the pyrogenic decomposition cited above, since the action can be envisaged most readily as an addition of the radicals $\cdot CH{:}C(CH_3)_2$ and H to the olefin $CH_2{:}C(CH_3)_2$.

The second process converts butylene into butadiene by the elimination of hydrogen, and is identical in type with the original pyrogenic decomposition. It is also analogous to the pyrogenic decomposition of benzene to diphenyl and hydrogen : $2C_6H_6 \longrightarrow C_6H_5{\cdot}C_6H_5 + H_2$. *A further application of this mechanism* will suffice to convert a mixture of ethylene and butadiene into hexatriene and then into benzene, and the further condensation of benzene with butadiene will give rise to naphthalene, anthracene, and other aromatic hydrocarbons.

A complete survey of the pyrogenic decomposition of the paraffin can thus be made, without the intervention of acetylene, on the basi

of a single well-established reaction of the olefins, *viz.*, the reversible addition and subtraction of hydrides of various types, since the polymerisation is merely a special case of reversible addition of a hydride, the olefin itself.

UNIVERSITY OF CAMBRIDGE.

LVII.—*Acid and Salt Effects in Catalysed Reactions. Part XIX. The Catalytic Activity of Chloroacetic Acid in the Hydrolysis of Ethyl Acetate.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

PREVIOUS observations (J., 1927, 2444) on the rate of hydrolysis of ethyl acetate with acetic acid as catalyst indicate that catalytic activity must be ascribed to both the acetic acid molecule and the acetate ion. When the concentration of the acetic acid is fixed and gradually increasing quantities of sodium acetate are added, the reaction velocity passes through a minimum, and it has been shown that the connexion between the velocity and the logarithm of the hydrogen-ion concentration is closely represented by the so-called catalytic catenary. When chloroacetic acid is used as catalyst, the relations presented by the velocity measurements are much less simple, and the co-ordination of the effects has necessitated a more complete examination of the catalytic behaviour of the acid.

With reference to the general equation $v = k_h[H^+] + k_a[A^-] + k_m[HA]$, it may be pointed out in the first place that the coefficients k_a and k_m for acetic acid are very small compared with k_h. Since k_m increases and k_a diminishes with increase in the ionisation constant of the catalysing acid, it was anticipated that little difficulty would be experienced in obtaining evidence for the catalytic activity of the chloroacetic acid molecule. It was found, however, that the formation of hydrochloric acid by chlorine hydrolysis of the chloroacetate interferes with the direct determination of the rate of ester hydrolysis when the chloroacetate is present in any considerable quantity. The incidence of this reaction sets a limit to the reduction of the hydrogen-ion concentration of the chloroacetic acid solutions by the addition of the corresponding salt for the purpose of obtaining conditions under which the velocity of the reaction is no longer dominated by the catalytic effect of the hydrogen ion. Quite apart from the chlorine hydrolysis, such conditions are much more difficult to realise with chloroacetic than with acetic acid, for the increase in the k_m value in passing from acetic to chloroacetic acid is very much less than the corresponding increase in the ionisation constant.

In further illustration of the difficulties which are met with in the present series of experiments, a comparison may be made between the catalytic effects which are associated with chloroacetic acid in the hydrolysis of ethyl acetate and in the acetone–iodine reaction. For the latter, the value of k_m/k_h is about 35 times as large as it is for the former reaction. Whilst, therefore, the determination of k_m for chloroacetic acid as catalyst in the acetone reaction can be readily effected with considerable accuracy, it is apparent that the evaluation of k_m for the ester hydrolysis may be seriously interfered with by those indirect catalytic influences which have been discussed by Dawson and Key (J., 1928, 1239, 1248) under the name of inert-salt effects and by Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169) under the name of primary and secondary kinetic salt effects.

In the investigation of the catalytic effects produced by chloroacetic acid or by the corresponding acid–salt mixtures, it has, therefore, been necessary to take account of the chlorine hydrolysis of the catalyst and of the influence of ionic environment on the catalytic coefficients and on the ionisation constant of the acid. With regard to the chlorine hydrolysis, it may be shown that this is negligible in experiments with 0·05 and 0·1*N*-chloroacetic acid when the concentration of the added chloroacetate does not exceed 0·2 mol. per litre. At greater concentrations, the hydrochloric acid formed not only interferes with the direct determination of the quantity of ester which has been hydrolysed, but by interaction with the sodium chloroacetate it alters the ratio of chloroacetate to chloroacetic acid and therefore the hydrogen-ion concentration of the solution. If, however, the hydrolysis of the ester is confined to the early stages of the reaction, it may be shown that this alteration does not appreciably affect the measurement of the required reaction velocity.

In order to ascertain the influence of the variations in ionic environment, experiments have been made with solutions of sodium chloride, which has no direct catalytic action in the hydrolytic change. In the application of the results of these experiments, it is assumed that the changes produced by sodium chloride in k_h and K are the same as those which may be attributed to equivalent quantities of sodium chloroacetate. Some such assumption is inevitable, although there can be little doubt that the inert-salt effects are not generally independent of the nature of the constituent ions. The results previously obtained with potassium, sodium, and lithium chlorides in the study of the acetone–iodine reaction with acetic acid as catalyst (*loc. cit.*) show, indeed, very clearly that the inert-salt effect is not solely determined by the ionic strength of the solution but that specific influences are involved.

By restricting the reaction to its early stages, two other minor sources of disturbance have been avoided, namely, those associated with the catalytic action of the acetic acid formed and with the retarding effect of the reverse reaction.

The experiments were made at 25° with solutions which contained 20 c.c. (0·206*M*) of ethyl acetate per litre, and in the first instance attention will be directed to those observations which seem to establish the existence of a catalytic effect attributable to the molecule of chloroacetic acid. In these experiments, the catalytic influence of the hydrogen ion was reduced by the use of solutions which contained sodium chloroacetate and chloroacetic acid in the ratio 10 : 1. In order to eliminate the effect of chlorine hydrolysis, parallel experiments were made with solutions which contained no ester. The corresponding pairs of solutions were titrated after equal intervals of time and the difference in the titres obviously affords a measure of the rate at which the ester is hydrolysed. The results of two such experiments are shown in Table I. The first row gives the time in minutes, the second shows the volume of 0·1*N*-sodium hydroxide required to neutralise 25 c.c. of the ester-free solution, whilst the third gives the figures for the ethyl acetate solution. The fourth row represents the difference (y) which affords a measure of the ester hydrolysed, and the fifth gives the values ($\times 10^4$) of the specific velocity $v = 1/t.\log_e a/(a - y)$ with $a = 51{\cdot}5$.

TABLE I.

$0{\cdot}1N$-$CH_2Cl{\cdot}CO_2H$ + $1{\cdot}0N$-$CH_2Cl{\cdot}CO_2Na$.

t (mins.)	4,100	9,900	15,500	21,260	28,470
C.c. alkali (no ester)	0·31	1·20	2·17	3·19	4·36
C.c. alkali (with ester)	0·93	2·62	4·41	6·20	8·40
y	0·62	1·42	2·24	3·01	4·04
v . 10^4	0·0295	0·0283	0·0287	0·0283	0·0287
				Mean	0·0285

$0{\cdot}05N$-$CH_2Cl{\cdot}CO_2H$ + $0{\cdot}50N$-$CH_2Cl{\cdot}CO_2Na$.

t (mins.)	4,060	9,850	15,450	21,220	28,460
C.c. alkali (no ester)	0·08	0·30	0·49	0·75	1·01
C.c. alkali (with ester)	0·53	1·44	2·31	3·19	4·31
y	0·45	1·14	1·82	2·44	3·30
v . 10^4	0·0216	0·0227	0·0233	0·0229	0·0233
				Mean	0·023

From the above table it is apparent that the hydrolysis of the ester proceeds in accordance with the equation for a unimolecular change with a constant catalytic factor. The collective results obtained in the present series of experiments afford no evidence of a measurable catalytic effect which might be attributed to the chloroacetic anion. This accords with the fact that the catalytic activity of the anion of the much weaker acetic acid is already very

small (see Dawson and Lowson, *loc. cit.*). Since, moreover, the experimental results with acetic acid as catalyst leave no room for a measurable water effect, it follows that the mean value of the specific velocity v affords a measure of the sum of the effects due to the hydrogen ion (v_h) and the chloroacetic acid molecule (v_m), or

$$v = v_h + v_m = k_h[H^+] + k_m[HA] = (k_h - k_m)[H^+] + k_m c \quad . \quad (1)$$

This equation may be used for the derivation of k_m provided that the value of k_h (Table II, col. 4) and the value of K (Table II, col. 6) from which $[H^+]$ is derived by means of the equation $[H^+] = k(c - [H^+])/[A^-]$ are those which correspond with the salt concentration of the solution under investigation. For the first experiment ($1N$-salt), $k_h = 8{\cdot}14 \times 10^{-3}$ and $K = 2{\cdot}40 \times 10^{-3}$ (compare Table II), whence $k_m = 0{\cdot}090 \times 10^{-4}$. For the second experiment ($0{\cdot}5N$-salt), $k_h = 7{\cdot}32 \times 10^{-3}$ and $K = 2{\cdot}53 \times 10^{-3}$, whence $k_m = 0{\cdot}095 \times 10^{-4}$.

The values of k_m derived in this way are in close agreement and would seem to show that the undissociated chloroacetic acid has a measurable catalytic effect. For our purpose the value of k_m may be taken as $0{\cdot}09 \times 10^{-4}$, and in accordance with the evidence afforded by previous observations on the acetone–iodine reaction, which show that the catalytic activity of the acetic acid molecule and of the acetic anion varies but slightly with the salt concentration, it is probable that this value is not appreciably affected by the ionic environment.

Dependence of k_h *and* K *on the Reaction Medium.*—On the assumption that the variations in k_h and K are independent of the nature of the uni-univalent salt which is present in the solutions, these variations have been derived from reaction-velocity measurements in sodium chloride solutions. To obtain the required values of k_h, measurements were made with $0{\cdot}01N$-hydrochloric acid as catalyst, and the results are summarised thus :

NaCl (mols./litre)	0	0·05	0·2	0·5	1·0	2·0	3·0	4·0
$k_h \cdot 10^3$	6·47	6·57	6·87	7·35	8·09	9·85	11·80	14·10

These values of k_h are in close agreement with those given by Harned and Hawkins (*J. Amer. Chem. Soc.*, 1928, **50**, 85) from experiments with $0{\cdot}1N$-hydrochloric acid as catalyst. The relation between k_h and the salt concentration is represented by a straight line if the latter is not much greater than 2 mols. per litre, but in more concentrated solutions the velocity increases somewhat more rapidly. Similar relations have already been noted in corresponding experiments with the acetone–iodine reaction.

The variations in K have been derived by combining the hydrochloric acid experiments with a corresponding series in which

0·1*N*-chloroacetic acid was used as catalyst. In Table II, col. 1 gives the concentration of the sodium chloride, col. 3 the specific reaction velocity $v = 1/t \, . \log_e a/(a - y)$, col. 4 the value of k_h given by the smooth curve which represents the results obtained with hydrochloric acid, col. 5 the hydrogen-ion concentration derived from $[H^+] = (v - k_m c)/(k_h - k_m)$ (compare equation 1), and col. 6 the ionisation constant $K = [H^+]^2/(c - [H^+])$. In addition the ionic strengths of the various solutions are shown in col. 2. Since the ionisation constant varies rapidly with the salt concentration in dilute solutions, particular attention has been given to the influence of small quantities of sodium chloride.

TABLE II.

0·1*N*-$CH_2Cl·CO_2H$ + *x*NaCl.

x.	μ.	$v \, . \, 10^4$.	$k_h \, . \, 10^3$.	$[H^+]$.	$K \, . \, 10^3$.
0	0·012	0·775	6·50	0·0118	1·58
0·01	0·022	0·799	6·52	0·01215	1·68
0·02	0·032	0·816	6·53	0·0124	1·75
0·03	0·042	0·836	6·55	0·01265	1·83
0·04	0·052	0·845	6·57	0·01275	1·86
0·05	0·063	0·875	6·58	0·0132	2·01
0·10	0·11	0·918	6·66	0·01365	2·16
0·20	0·21	0·970	6·82	0·0141	2·31
0·30	0·31	1·005	6·98	0·0143	2·39
0·50	0·51	1·085	7·32	0·0147	2·53
1·0	1·01	1·177	8·14	0·01435	2·40
2·0	2·01	1·304	9·90	0·0131	1·98
3·0	3·01	1·370	11·80	0·01155	1·51
4·0	4·01	1·330	14·10	0·00938	0·97

The concentration of the ester in the above experiments was for the most part 20 c.c. per litre, but on account of "salting out" this was reduced to 8·0 c.c. per litre in the case of the 3 and 4*M*-salt solutions. That this reduction in the ester concentration does not affect the comparability of the results is shown by the fact that the observed velocity for the 2*M*-salt solution is very nearly the same for the two ester concentrations.

The variation of *K* with the salt concentration is similar to that shown by corresponding data for the acetone–iodine reaction. In so far as the dilute salt solutions are concerned, the two series of data are not, however, strictly comparable, for the acetone experiments were made with solutions which contained a small quantity of potassium iodide.

With regard to the accuracy of the *K* values, it should be noted that the hydrogen-ion concentrations from which these are derived depend on measurements of the reaction velocity with both hydrochloric and chloroacetic acids. If the possible error in the observed velocity is assumed to be 1%, it is evident that the error in the individual values of *K* may be as high as 4%. The values derived

from K–x graphs are probably more accurate than this, and such smoothed values are actually used in applying these preliminary observations to the interpretation of the experiments which are to be described.

Since the ionic strength of the sodium chloride-free solution is *0·012*, it may be anticipated that the value of K for a solution in which the ionic effects are negligible will be appreciably less than the first recorded value, *viz.*, $1·58 \times 10^{-3}$. In this connexion, attention may be directed to the method described by Dawson, Hall, and Key (J., 1928, 2844) for the determination of the limiting value of K for reaction velocity data. This method when applied to the data for chloroacetic acid and the acetone–iodine reaction gave for the limiting value $K_0 = 1·51 \times 10^{-3}$. By its application to the data for the hydrolysis of ethyl acetate, we obtain $K_0 = 1·48 \times 10^{-3}$. These results suggest that the value of the ionisation constant of chloroacetic acid in very dilute solution may be taken as $K_0 = 1·5 \times 10^{-3}$.

Catalytic Activity of Chloroacetic Acid in Presence of Chloroacetate.—Experiments with acid–salt mixtures of the series cCH$_2$Cl·CO$_2$H + xCH$_2$Cl·CO$_2$Na (c constant, x variable) show that the reaction velocity falls continuously as the concentration of the chloroacetate increases. On account of chlorine hydrolysis, the investigation of such mixtures cannot, however, be extended to solutions for which x is much greater than unity.

The results for two series of constant-acid mixtures are recorded in Table III. The first line of figures gives x; the second and third the corresponding values of k_h and K; the fourth shows the observed velocities given by $v = 1/t \,.\, \log_e a/(a - y)$, and the fifth the velocities calculated from equation (1).

TABLE III.

$0·1N$-CH$_2$Cl·CO$_2$H + xN-CH$_2$Cl·CO$_2$Na.

x	0	0·02	0·05	0·1	0·2	1·0
$k_h \,.\, 10^3$	6·50	6·53	6·58	6·66	6·82	8·14
$K \,.\, 10^3$	1·60	1·80	2·00	2·15	2·35	2·40
$v \,.\, 10^4$ obs.	0·775	0·413	0·234	0·142	0·086	0·0285
$v \,.\, 10^4$ calc.	0·780	0·426	0·245	0·146	0·088	0·0285

$0·05N$-CH$_2$Cl·CO$_2$H + xN-CH$_2$Cl·CO$_2$Na.

x	0	0·02	0·05	0·1	0·2	0·5
$k_h \,.\, 10^3$	6·50	6·53	6·58	6·66	6·82	7·32
$K \,.\, 10^3$	1·55	1·80	2·00	2·15	2·35	2·50
$v \,.\, 10^4$ obs.	0·523	0·224	0·122	0·071	0·041	0·023
$v \,.\, 10^4$ calc.	0·527	0·236	0·126	0·073	0·044	0·023

From the general agreement between the observed and the calculated velocity it may be inferred that the specific rate of hydrolysis

of the ester is determined by the sum of the catalytic effects which are due to the hydrogen ion and the chloroacetic acid molecule. If the variations of k_h and K with the ionic concentration are not taken into account, the differences between the observed and calculated velocities are very large, as may be seen when the latter are derived from the limiting values $k_h = 6{\cdot}50 \times 10^{-3}$ and $K = 1{\cdot}5 \times 10^{-3}$. For the successive experiments with $0{\cdot}1N$-chloroacetic acid in Table III these calculated velocities are 0·756, 0·368, 0·188, 0·102, 0·056, and 0·018.

In further support of the interpretation given to the experiments of Table III, measurements have also been made with solutions of chloroacetic acid–chloroacetate mixtures in which the total salt concentration was kept constant at 1 mol. per litre by the addition of sodium chloride. In these circumstances the inert-salt factor remains unchanged and the observed reaction velocities can be satisfactorily expressed in terms of equation (1) with constant values of $k_h = 8{\cdot}14 \times 10^{-3}$ and $K = 2{\cdot}40 \times 10^{-3}$ (compare Table II), as may be seen from Table IV.

TABLE IV.

$0{\cdot}1N$-$CH_2Cl{\cdot}CO_2H$ + xN-$CH_2Cl{\cdot}CO_2Na$ + $(1 - x)N$-NaCl.

x	0	0·02	0·05	0·1	0·2	1·0
$v \cdot 10^4$ obs.	1·177	0·656	0·353	0·195	0·104	0·0285
$v \cdot 10^4$ calc.	1·175	0·653	0·354	0·195	0·105	0·0285

Influence of Concentration on the Catalytic Activity of Free Chloroacetic Acid.—Variations in the catalysing power of an acid with its concentration were first used by Dawson and Powis (J., 1913, **103**, 2135) for the determination of the coefficients which express the catalytic activity of undissociated acid molecules. The numbers derived in this way for the acetone–iodine reaction have since been confirmed by experiments with acid–salt mixtures. It should be clearly recognised, however, that the successful application of the method depends on the magnitude of the ratio k_m/k_h. The measured velocity represents the sum of the partial velocities due to the ionised and to the un-ionised acid, and since the ionic strength of the solution, and therefore the ionisation constant of the acid, increases with the total concentration of the acid, it follows that the increase in the catalytic effect due to the ionised acid will be greater than it would have been if the ionisation constant of the acid were independent of its concentration. If k_m/k_h is relatively large, this variation of K may not interfere very much with the determination of k_m, but will obviously do so if k_m/k_h is very small. For this reason, the variation of the velocity of hydrolysis of ethyl acetate with the concentration of the catalysing acid cannot be used for the determination of k_m for

chloroacetic acid, although this method is readily applicable in the case of the acetone–iodine reaction. Furthermore, there is reason to believe that the changes in K due to ionic environment cannot be assumed to remain the same when a univalent metal ion is replaced by the stoicheiometrically equivalent quantity of "hydrogen" ion. In these circumstances it is not possible to calculate the velocities for the chloroacetic acid at different concentrations with the requisite degree of accuracy. On the other hand, the observed velocities may be utilised for the derivation of K values by the application of equation (1). The results obtained with $k_h = 6{\cdot}50 \times 10^{-3}$ and $k_m = 0{\cdot}09 \times 10^{-4}$ are as follows :

c	0·01	0·02	0·05	0·1	0·2
$v \,.\, 10^4$ obs.	0·209	0·312	0·523	0·775	1·140
$K \,.\, 10^3$	1·51	1·50	1·52	1·58	1·64

The anticipated increase in the ionisation constant is thus actually found, but the increase is small and too much significance cannot be attached to the individual values. The difficulties associated with the auto-ionising influence which has been referred to may, however, be obviated by using a moderately concentrated salt solution as solvent instead of water. Under these conditions the ionisation constant of the acid should be independent of its concentration if this is not made too large. The experimental results for a series of chloroacetic acid solutions with $1N$-sodium chloride as solvent are summarised below. The calculated reaction velocities are those derived from equation (1), with $k_h = 8{\cdot}14 \times 10^{-3}$, $K = 2{\cdot}40 \times 10^{-3}$, and $k_m = 0{\cdot}09 \times 10^{-4}$.

TABLE V.

cN-$CH_2Cl{\cdot}CO_2H$ + $1N$-NaCl.

c	0·005	0·01	0·02	0·05	0·1	0·2	0·3
$v \,.\, 10^4$ obs.	0·202	0·314	0·470	0·804	1·177	1·70	2·09
$v \,.\, 10^4$ calc.	0·201	0·314	0·476	0·803	1·175	1·70	2·11

The differences between the observed and calculated velocities in this series are well within the probable errors of experiment, and it would therefore seem that the catalytic activity of chloroacetic acid can be represented in terms of equation (1) with a constant value of the ionisation constant when the nature of the solvent is such that the ionic environment is sensibly constant.

Summary.

The foregoing series of experiments shows that the catalytic effects produced by chloroacetic acid in the hydrolysis of ethyl acetate can be expressed by $v = k_h[H^+] + k_m[HA]$, provided that the variation of k_h and K with the ionic environment is taken into account. The effect of the chloroacetate ion appears to be very small. In sodium

chloride solutions of gradually increasing concentration, the value of k_h shows a continuous increase, whilst K passes through a maximum at about 0·5M-concentration.

When constancy of ionic environment is provided for, the catalytic effects produced by free chloroacetic acid and by mixtures of this with chloroacetate can be satisfactorily explained in terms of fixed values of the ionisation constant and of the catalytic coefficients. The ratio k_m/k_h for chloroacetic acid in the hydrolysis of ethyl acetate is about 1/700, compared with 1/20 for the catalysing action of the acid in the acetone–iodine reaction.

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LVIII.—*Optical Activity and the Polarity of Substituent Groups. Part X. Influence of Ionisable Groups on the Rotatory Power of* l-*Menthyl Benzoate.*

By H. GORDON RULE and W. EOGHAN MACGILLIVRAY.

THE changes in the rotatory powers of optically active acids and bases consequent upon ionisation have been discussed in Part VI of this series (J., 1927, 54), in which attention was drawn to the fact that the characteristic influence of groups such as $\cdot CO_2H$ and $\cdot NH_2$ is often reversed when these are present in the ionised state. A similar reversal on ionisation occurs in the directive power of the groups upon benzene substitution (compare Flürscheim, *Chem. and Ind.*, 1926, **45**, 143; Ing and Robinson, J., 1926, 1655; Goss, Ingold, and Wilson, *ibid.*, p. 2440).

Effects of this type are of special interest in connexion with the menthyl esters of *o*-substituted benzoic acids, among which *m*-directive substituents raise, and *o*, *p*-directive groups lower the molecular rotation. One example of the influence of an ionised grouping on the rotatory power of menthyl benzoate is already available. Kenyon and Pickard (J., 1915, **107**, 54, 58), in investigating the optical rotatory powers of a number of menthyl derivatives prepared by Cohen, have recorded values for the sodium and magnesium salts of menthyl hydrogen phthalate which are much lower than those for the unsubstituted benzoate. By analogy, it has been predicted (Part VI, *loc. cit.*) that the *o*-dimethylaminobenzoic ester should exhibit an enhanced rotation in acid solution.

The present communication contains an account of the menthyl esters of hydroxy-, amino-, and dimethylamino-benzoic acids. The *o*-, *m*-, and *p*-dimethylamino-derivatives were among the large number of substituted benzoic esters prepared by Cohen (J., 1914,

105, 1892), who encountered great difficulty in their purification and finally examined them in the form of viscous, strongly coloured liquids. The rotatory powers of these liquids were not changed by solution in light petroleum, followed by precipitation as the liquid hydrochloride and subsequent removal of hydrogen chloride (Cohen, *loc. cit.*). During the present investigation the main difficulty was found in obtaining a good yield of the esters, especially of the *m*- and *p*-isomerides. The *o*-compound was prepared as a coloured product of somewhat higher rotatory power than that recorded by Cohen, the value being unaltered after attempted purification by the above method. On distillation in a high vacuum, however, the mixture separated into a colourless low-melting solid (about two-thirds of the total) and a highly coloured glass. The rotatory power of the solid was nearly double that recorded by Cohen, and was confirmed on a specimen prepared by a different method (see p. 407). The glassy residue had a correspondingly low rotation. It was not found possible to obtain the *m*- and *p*-isomerides in a state of optical purity.

The influence of ionisation was determined by measuring the rotatory powers of the four basic esters (*a*) in alcohol, and (*b*) in alcohol containing an equivalent of hydrogen chloride; the three acid esters were examined (*a*) in alcohol, (*b*) in alcohol containing an equivalent of sodium or potassium ethoxide, and (*c*) in piperidine. To complete the comparison it was necessary to know the rotatory powers of menthyl benzoate and also of menthyl hydrogen phthalate and its sodium salt in 5% alcoholic solutions. This information could not be discovered in the literature, and the preparation of these esters was therefore repeated. The rotatory power of menthyl benzoate in alcohol was found to be practically unaffected by the presence of as much as four equivalents of hydrogen chloride or of sodium ethoxide (see Table I, i). Wherever possible, the rotatory powers were determined for the wave-lengths 6708, 5893, 5461, and 4358 Å.U., and at approximately 20°.

Influence of Substituents.

As with other menthyl esters of this type, the compounds described in this communication exhibit normal and complex dispersion, the graph of $1/\alpha$ plotted against λ^2 deviating appreciably from the linear. The *salicylate*, on account of its abnormally high rotation, was examined in the homogeneous state over the temperature range 20—100°; the dispersion was complex throughout and the rotation fell slightly but continuously with rise of temperature.

From the tables it is seen that the *o*-derivatives differ considerably in rotatory power from the unsubstituted ester. In these com-

TABLE I.

(i) 1-*Menthyl benzoate.*

Solvent.	*l.*	*c.*	$[M]_{5461}$.
Benzene *	2	5·032	−280·5°
Alcohol	2	5·031	275·1
,, + 4HCl	2	5·069	274·7
,, ,, (1 hr. later)			274·7
,, + 4NaOEt	2	5·001	275·8
,, ,, (30 mins. later)			272·7

(ii) 1-*Menthyl* o-*dimethylaminobenzoate.*

Solvent.	*l.*	*c.*	$[M]_{5461}$.
Alcohol	1	4·746	−250°
,, + HCl	1	3·736	292

(iii) 1-*Menthyl aminobenzoates.*

Isomeride.	Solvent.	*l.*	*c.*	$[M]_{5461}$.
o-	Alcohol	1	5·009	−313°
	,, + HCl	1	5·001	290
m-	Alcohol	1	3·186	281
	,, + HCl	1	1·583	271
p-	Alcohol	1	5·032	257
	,, + HCl	1	3·566	262

(iv) 1-*Menthyl hydroxybenzoates.*

Isomeride.	Solvent.	*l.*	*c.*	$[M]_{5461}$.
o-	(Homogeneous, 20°)	1	—	−333·2°
	(,, 100°)	1	—	330·5
	Alcohol	2	5·163	299
	,, + NaOEt	2	4·880	267
	,, + KOEt	2	5·680	246
	Piperidine	2	5·445	286
†*m*-	Alcohol	1	7·735	266
	,, + NaOEt	1	5·608	235
	Piperidine	1	8·815	222
†*p*-	Alcohol	1	5·144	250
	,, + NaOEt	1	4·873	241
	Piperidine	1	4·216	219

(v) 1-*Menthyl hydrogen phthalate.*

Solvent.	*l.*	*c.*	$[M]_{5461}$.
Benzene	2	4·725	399·0° ‡
Alcohol	2	5·128	345·6
,, (Na salt)	1	5·382	260·5
,, (Mg salt)		(5% approx.)	212·0 §

* Kenyon and Pickard, *loc. cit.*, record −276·5°.

† These isomerides could only be isolated in the form of somewhat coloured viscous liquids, the *p*-compound being almost a glass. There is therefore some doubt as to their purity.

‡ For λ_{5893}, $[M] = -331·9°$ (Cohen, J., 1916, **109**, 232, records $[M]_{5893} = -332·4°$ in benzene, $c = 5$).

§ Kenyon and Pickard, *loc. cit.*

pounds the introduction of an *o*-carboxyl group results in a marked rise in rotation, which is changed to a fall when the substituent ionises to ·COO′. On the other hand, an *o*-dimethylamino-group depresses the rotatory power of the benzoate, but raises the value when present in acid solution as $·NMe_2H^·$. The optical changes are

therefore related to the orienting power of the groups in benzene substitution, the *m*-directive carboxyl and dimethylammonium radicals raising the rotation and the *o,p*-directive dimethylamino-group and carboxyl anion lowering the value.

Minor changes in the *o*-carboxyl group may also be brought about by esterification. Here again the relative influence is in agreement with the directive power of the group X, as becomes evident on comparing the percentages of *m*-compound formed on nitration of C_6H_5X with the values for the rotatory powers of the menthyl alkyl phthalates recorded by Cohen, Woodruffe, and Anderson (J., 1916, **109**, 222) :

X.	CO_2H.	CO_2Me.	CO_2Et.	H.	(COO′)
m-Compound, % ...	80·2	73·2	68·4	—	(*o*, *p*)
$[M]_D$	−332°	−268°	−254°	−239°	(192°)

Among the large number of menthyl and *sec.*-β-octyl esters of *o*-substituted benzoic acids now known, the salicylic and anthranilic esters under examination are the only ones in which the presence of an *o*, *p*-directive substituent is found to raise the rotatory power. The influence in these cases may therefore be an abnormal one due to the co-ordination of the carboxylic keto-group with hydrogen of the hydroxyl or amino-group (Sidgwick, J., 1920, **117**, 402; Sidgwick and Ewbank, J., 1921, **119**, 979). This possibility appears to be supported by the low boiling points of the *o*-isomerides as compared with those of the *m*- and *p*-compounds, thus :

l-Menthyl ester.	B. p.	*l*-Menthyl ester.	B. p.
Anthranilate	156°/0·3 mm.	Salicylate	156°/0·5 mm.
m-Aminobenzoate	168°/1·8 mm.	*m*-Hydroxybenzoate	182°/1·2 mm.
p-Aminobenzoate	175°/0·2 mm.	*p*-Hydroxybenzoate ...	178°/0·1 mm.

and also by the relative insolubility of the salicylic ester in hydroxylic solvents (compare Sidgwick, *loc. cit.*). Experiment showed that menthyl salicylate at room temperature required seven times its volume of absolute methyl alcohol or six times its volume of rectified spirits (96%) for complete miscibility : it is miscible in all proportions with absolute ethyl alcohol, benzene, or light petroleum.

Even on the assumption that the two *o*-substituents are present in these esters as part of a chelate ring, it would still be anticipated that the characteristic effects of the electrical charges (−O′ and −NH_3˙) would make themselves evident on ionisation. This expectation is borne out by the above figures. The amino-ester in the form of its hydrochloride has a rotation of $[M]_{5461}$ = −290°, comparable with that found for the hydrochloride of the dimethylamino-ester (−292°), and considerably higher than that of menthyl benzoate (−275°). On the other hand, the salicylic ester in the presence of an equivalent of sodium ethoxide exhibits a rotatory power (−267°)

which is lower than that of the benzoate. This last figure is not so low as was anticipated by comparison with the value (−260°) recorded in Table I (v) for the alcoholic solution of sodium menthyl phthalate, possibly because part of the salicylate exists under the conditions of experiment as the free chelated hydroxy-ester or as the chelate form of the sodium derivative.

Sidgwick and Brewer (J., 1925, **127**, 2381) have concluded that potassium salts of this type are less prone to form chelate derivatives than the corresponding sodium salts. For this reason the salicylic ester was next examined in the presence of an equivalent of potassium ethoxide. In this case a much lower rotation (−246°) was observed. Hence, although the parent anthranilic and salicylic esters behave abnormally, the rotations of the ionised compounds are in agreement with the regularities previously established.

The normal effect exhibited by the *o*-dimethylamino-grouping supports the conclusions of Pfeiffer, Angern, and Wang (*Z. physiol. Chem.*, 1927, **164**, 182), who find that the keto-group in diketopiperazines co-ordinates with primary and secondary amines and with the aminobenzoic acids, but not with tertiary amines or with the dimethylaminobenzoic acids.

A discussion of these results from the standpoint of the electronic theory is reserved, pending the completion of allied lines of research.

EXPERIMENTAL.

l-*Menthyl salicylate* was prepared in the usual way from the acid chloride and menthol. The rotatory power of the crude ester rose slowly on fractionation in a high vacuum, remaining constant after the third repetition. The pure ester was obtained in better yield (60%) by dissolving the crude product in warm methyl alcohol and cooling to −15°; it is a viscous, colourless, and odourless oil, b. p. 156°/0·5 mm. (Found: C, 73·9; H, 8·9. $C_{17}H_{24}O_3$ requires C, 73·9; H, 8·7%).

l-*Menthyl* m-*hydroxybenzoate*. Thionyl chloride (2 equivs.) was added in small portions at 0° to sodium *m*-hydroxybenzoate (1 equiv.; carefully dried below 50°). When the vigorous action had ceased, the excess of thionyl chloride was removed under diminished pressure. The crude acid chloride was treated with menthol (1 mol.) and pyridine, and maintained at 120° for 24 hours. Reaction appeared slow. The mixture was diluted with water, the ester extracted with ether, and dried over sodium sulphate. After removal of the solvent, any excess of menthol was distilled off in a vacuum. The *ester* distilled as a slightly coloured oil, b. p. 182°/1·2 mm. (Found: C, 73·6; H, 8·8%) (yield, 20% of theory). The rotatory power was not altered on repeated fractionation.

l-*Menthyl* p-*hydroxybenzoate*, prepared in the same way as the *m*-compound, but in poorer yield (10%), was isolated as a pale yellow oil, b. p. 178°/0·1 mm., which solidified to a transparent glass, and could not be obtained crystalline. The rotatory power was unchanged on further fractionation (Found: C, 73·5; H, 8·9%). Both the *m*- and *p*-hydroxy-esters were miscible in all proportions with methyl or ethyl alcohol and with rectified spirits.

l-Menthyl anthranilate could not be prepared directly from anthranilic acid, nor could the chloride of the acid be isolated by means of thionyl chloride (compare McMaster and Ahmann, *J. Amer. Chem. Soc.*, 1928, **50**, 146). The ester was readily obtained in almost theoretical yield by the reduction of optically pure *l*-menthyl o-nitrobenzoate (Cohen, J., 1914, **105**, 1892), by means of tin and hydrochloric acid. The amino-ester was precipitated from the dried ethereal solution with gaseous hydrogen chloride, and the solid *hydrochloride* recrystallised from alcohol containing a little hydrogen chloride until of constant rotatory power; m. p. 150—170° (indefinite) (Found: Cl, 11·4. $C_{17}H_{26}O_2NCl$ requires Cl, 11·4%); it was sparingly soluble in cold alcohol, giving a violet fluorescent solution.

Free l-*menthyl anthranilate* was obtained from the salt as a colourless solid, m. p. 62·5—63·5°, b. p. 156°/0·33 mm. (Found: N, 5·3. $C_{17}H_{25}O_2N$ requires N, 5·1%). It dissolves readily in alcohol, giving a violet fluorescent solution. Unlike the *m*- and *p*-isomerides, the o-amino-ester dissolves readily in dilute aqueous acids.

l-*Menthyl* m-*aminobenzoate*. After unsuccessful attempts to prepare the ester directly from *m*-aminobenzoic acid, it was eventually obtained from pure *l*-menthyl *m*-nitrobenzoate by reduction with titanous chloride in boiling alcoholic solution. Dry hydrogen chloride precipitated the ester from ethereal solution as the hydrochloride in the form of a yellowish-brown oil. This was treated with sodium carbonate to give the free ester, which was purified again through the hydrochloride. l-*Menthyl* m-*aminobenzoate* distilled as an almost colourless oil, b. p. 168°/1·8 mm (yield 40%)(Found: N, 5·3. $C_{17}H_{25}O_2N$ requires N, 5·1%).

l-*Menthyl* p-*aminobenzoate* was prepared in the same way as the *m*-derivative, but only in 10% yield, probably owing to hydrolysis during reduction. The compound decomposes slightly on distillation (b. p. 175°/0·2 mm.), the yellow distillate having a slight smell of menthol (Found: N, 5·3%). The ester forms a solid hydrochloride, melting indefinitely in the neighbourhood of 200°, by means of which it was purified. The salt easily loses hydrogen chloride in aqueous-alcoholic solution.

Both *m*- and *p*-amino-ester hydrochlorides dissolve in concen

trated hydrochloric acid, but are precipitated on addition of a small amount of water.

l-*Menthyl* o-*dimethylaminobenzoate* was prepared from *o*-dimethylaminobenzoic acid by way of the acid chloride (compare Cohen and Dudley, J., 1910, **97**, 1737). The product was dissolved in dilute hydrochloric acid, and any unchanged menthol extracted with ether. The aqueous liquor was made alkaline, the free ester removed with ether, and the extract dried over sodium sulphate. On evaporation of the solvent a highly coloured viscous mass resulted which had a rotatory power ($\alpha_D^{16°}$ $-51{\cdot}6°$, $l = 1$) somewhat higher than that recorded by Cohen and Dudley ($\alpha_D = -10{\cdot}24°$, $l = 0{\cdot}302$). This rotatory power was not changed when the ester in ethereal solution was kept over animal charcoal and subsequently precipitated from light petroleum as the liquid hydrochloride, as recommended by the above authors. The product was therefore distilled in a high vacuum, and thus separated into a pale yellow oil, b. p. 170—171°/0·6 mm., $\alpha_{5893}^{16°}$ $-35{\cdot}67°$ ($l = 0{\cdot}5$), forming about two-thirds of the total volume, which slowly solidified in the receiver, and a highly coloured glassy residue ($\alpha_{5893}^{16°}$ $-0{\cdot}61°$ in benzene, $l = 1$, $c = 2{\cdot}18$). The rotatory power of the original mixture was approximately the mean of the values found for the two fractions. The crude solid ester, m. p. 35—75° (mainly 35—38°), was purified with considerable loss, owing to its high solubility, from light petroleum at $-15°$, and then had m. p. 36—37° (Found : C, 75·3; H, 9·9; N, 5·1. $C_{19}H_{29}O_2N$ requires C, 75·2; H, 9·6; N, 4·6%). (An unidentified solid of higher m. p., and containing sulphur, was isolated as a by-product.) The somewhat high value found for nitrogen has since been traced to the tendency of the dimethylamino-esters on combustion to yield nitrogen admixed with a small amount of combustible gas, probably methane or ethane, which is exceedingly difficult to convert quantitatively into carbon dioxide and water.

In view of the unexpectedly high rotatory power of this ester, the compound was prepared by another method. Methyl *o*-dimethylaminobenzoate (14 g.) was added to *l*-menthol (25 g.) in which sodium (0·05 atom) had been dissolved (compare suggestion of Verley, *Bull. Soc. chim.*, 1927, **41**, 788). The mixture was maintained at 150—160° in a distilling flask, and a slow current of dry air drawn through the apparatus. Methyl alcohol, menthene, and menthol slowly distilled over, and after 3 hours the residue in the flask was distilled in a vacuum, giving *l*-menthyl *o*-dimethylaminobenzoate (8 g.), b. p. 170°/0·2 mm. The ester solidified on standing, and on repeated recrystallisation from light petroleum possessed the same m. p. and rotatory power as the product obtained as above. The authors wish to thank Mr. C. F. Campbell for carrying out this preparation.

Attempts to repeat the preparation of the *m*- and *p*-dimethylaminobenzoic esters (see Cohen and Dudley, *loc. cit.*) were unsuccessful, leading to the formation of inseparable mixtures of varying rotatory power.

Menthyl hydrogen phthalate was prepared according to the method of Arth (*Ann. Chim. Phys.*, 1886, **7**, 485).

Measurements of Rotatory Power.

The rotatory powers (determined as in previous papers) are given in Table II. *An asterisk attached to the first column indicates $l = 2$; otherwise $l = 1$. Where sodium or potassium ethoxide or hydrogen chloride is mentioned, one equivalent was employed.*

TABLE II.

l-*Menthyl salicylate* (homogeneous).

t.	*d.*	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.
20°	1·0467	208·9°	278·8°	333·2°	590·3°
40	1·0319	208·6	278·3	332·4	588·3
60	1·0170	208·3	277·7	331·9	586·4
80	1·0022	207·8	277·1	331·2	584·2
100	0·9877	207·4	276·5	330·5	582·1

l-*Menthyl hydroxybenzoates* (at 20° approx.).

Isomeride.	Solvent.	c.	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.
*o-	Alcohol	5·163	192°	253°	299°	500°
	,, + NaOEt ...	4·880	176	228	267	(412)
	,, + KOEt ...	5·680	—	—	246	—
	Piperidine	5·445	183	241	286	498
m-	Alcohol	7·735	—	—	266	—
	,, + NaOEt ...	5·608	—	—	235	—
	Piperidine	8·815	—	—	222	—
p-	Alcohol	5·144	—	—	250	—
	,, + NaOEt ...	4·873	—	—	241	—
	Piperidine	4·216	—	—	219	—

Rotations of the above esters measured in the presence of ethoxide showed no decrease in value during the period of measurement or the succeeding half-hour.

l-*Menthyl aminobenzoates.*

Isomeride.	Solvent.	c.	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.
o-	Alcohol	5·009	210°	261°	313°	511°
	,, + HCl	5·001	187·5	240	289	483
m-	Alcohol	3·186	182	238	276	466
	,, + HCl	1·583	181	231	272	451
p-	Alcohol	5·032	175	224	257	—
	,, + HCl	3·566	176	227	262	—

l-*Menthyl dimethylaminobenzoate.*

Isomeride.	Solvent.	c.	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.
o-	Benzene	5·243	—	206	—	—
	Alcohol	4·746	151	206	250	419
	,, + HCl	3·736	192	251	292	482
	[illegible]	[illegible]	—	230	269	440

For rotatory powers of *l*-menthyl benzoate and *l*-menthyl hydrogen phthalate see Table I, (i) and (v).

Summary.

An investigation has been made of the alteration in the rotatory power of *l*-menthyl benzoate following nuclear substitution by dimethylamino-, amino-, hydroxy-, and carboxy-groups and their corresponding ionised forms.

The most definite variations are those found among the *o*-substituted esters. The optical properties of these derivatives are in agreement with the regularities previously established among *o*-esters of this kind. The groups CO_2H, $NMe_2H^{\cdot}$, and $NH_3^{\cdot}$, which orient to the *m*-position in benzene substitution, lead to an increased rotatory power, whereas the groups COO′, NMe_2, and O′, which are *o,p*-directive in type, lead to a fall in rotation. Minor changes in the *o*-carboxy-group, due to formation of methyl or ethyl esters (Cohen, Woodruffe, and Anderson, *loc. cit.*), also affect the rotation in the sense anticipated from this relationship, the rotatory power diminishing as the substituent becomes less *m*-directive in power.

Exceptional behaviour is exhibited by the hydroxyl and amino-groups in the un-ionised salicylic and anthranilic esters, both of which have abnormally high rotations. This is ascribed to the chelated condition of these compounds.

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UNIVERSITY OF EDINBURGH. [*Received, January 15th, 1929.*]

LIX.—*The Cobaltic Derivatives of $\beta\beta'\beta''$-Triaminotriethylamine.*

By FREDERICK GEORGE MANN.

$\beta\beta'\beta''$-TRIAMINOTRIETHYLAMINE, $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$, was first prepared by Ristenpart (*Ber.*, 1896, **29**, 2530), who showed that the presence of the three primary amine groups caused the fourth tertiary amine group to be neutral, since, for example, the base formed a trihydrochloride, $N(CH_2{\cdot}CH_2{\cdot}NH_2,HCl)_3$: in fact, all Ristenpart's derivatives are normal derivatives of a triacidic base. The chemistry of this polyamine was further investigated by Mann and Pope (*Proc. Roy. Soc.*, 1925, *A*, **109**, 444; J., 1926, 482), who showed that it furnished, when recrystallised from concentrated hydrochloric acid, a tetrahydrochloride; this, however, on exposure

to air slowly lost hydrogen chloride, giving Ristenpart's trihydrochloride. Two distinct series of derivatives were obtained from the tri- and the tetra-hydrochloride respectively. Many complex salts of the amine with various metals were also prepared; in all these salts, the base co-ordinates as a tetra-amine, occupying four co-ordination positions, and these were the first complex salts of an aliphatic tertiary amine to be isolated. For instance, if one molecule of triaminotriethylamine be denoted by the symbol "tren," it was found that metals of co-ordination number 4 gave salts such as triaminotriethylaminenickelous thiocyanate, $[Ni\ tren](SCN)_2$, and *triaminotriethylamineplatinous* iodide, $[Pt\ tren]\,I_2$, whereas metals of co-ordination number 6 gave salts such as dichlorotriaminotriethylamineplatinic dichloride, $[Cl_2Pt\ tren]Cl_2$, and tristriaminotriethylaminebisnickelous tetraiodide, $[Ni_2\ tren_3]I_4$.

The complex salts of this amine with cobalt were subsequently investigated by Jaeger and Koets (*Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1). These authors apparently isolated no mononuclear derivative of cobalt, but by treating aquochlorobisethylenediaminecobaltic chloride with the tetra-amine they prepared the remarkable complex salt, hexaethylenediaminebistriaminotriethylaminetricobaltic nonaiodide, $[Co_3\ en_6\ tren_2]I_9$. In this compound the triaminotriethylamine is co-ordinated by the three primary amine groups alone, the tertiary amine group remaining free and unco-ordinated. The authors have discussed the stereochemistry of this compound in detail, and have described its probable symmetric configuration.

It is now shown, however, that more simple mononuclear compounds of this tetra-amine with cobalt can be prepared, since the metal furnishes salts of the normal diacidotetrammino-type, *e.g.* *dithiocyanato-ββ'β''-triaminotriethylaminecobaltic monothiocyanate* $[(SCN)_2Co\ tren]\,SCN$. This compound is thus of the same genera type as the platinic salt above: the base is again co-ordinated by all four amine groups, and the complex ion, having a plane of symmetry, cannot be resolved into optically active forms. Severa derivatives of this complex ion have been described, and they ar all highly crystalline stable salts.

EXPERIMENTAL.

Dithiocyanatotriaminotriethylaminecobaltic Monothiocyanate Mono hydrate, $[(SCN)_2Co\ tren]SCN,H_2O$.—A mixture of roseo-cobalt chloride (4 g.) and triaminotriethylamine trihydrochloride (5·6 g is added to water (300 c.c.), and the whole boiled under reflux fo 6 hours. The clear deep red solution is thrice evaporated to sma bulk with intermediate addition of water, and the final solutio

chilled and diluted with concentrated potassium thiocyanate solution. A fine brown product separates and after a short time is followed by a deep red crystalline precipitate. After standing over-night, the mixture is collected, and twice recrystallised from hot water. The *monothiocyanate monohydrate* is thus obtained in deep red needles, m. p. 208—210° (decomp.), readily soluble in hot, but only slightly soluble in cold, water (Found: C, 27·2; H, 5·1; N, 24·8; S, 23·9. $C_9H_{18}N_7S_3Co,H_2O$ requires C, 27·2; H, 5·0; N, 24·7; S, 24·2%).

The *mononitrate monohydrate*, $[(SCN)_2Co\ tren]NO_3,H_2O$, is prepared by treating a cold supersaturated solution of the monothiocyanate with very dilute nitric acid. The crystalline nitrate rapidly separates, and is obtained by recrystallisation from hot water, in which it is readily soluble, in large deep red prisms, m. p. 226° (decomp.) (Found: C, 24·2; H, 5·0; N, 24·5; S, 16·2. $C_8H_{18}O_3N_7S_2Co,H_2O$ requires C, 23·9; H, 5·0; N, 24·4; S, 16·0%).

The anhydrous *monochloride*, $[(SCN)_2Co\ tren]Cl$, is prepared similarly by treating a cold aqueous solution of the monothiocyanate with dilute hydrochloric acid. A small crop of the crystalline monochloride separates over-night and, after recrystallisation from hot water, is obtained in fine deep red crystals, m. p. 225—226° (decomp.) (Found: N, 23·8; Cl, 9·9; S, 18·1. $C_8H_{18}N_6ClS_2Co$ requires N, 23·6; Cl, 9·9; S, 18·0%).

The *chloroplatinate*, $[(SCN)_2Co\ tren]_2PtCl_6$, is best prepared by adding an aqueous solution of the monothiocyanate, containing dilute hydrochloric acid, to a solution of chloroplatinic acid. The chloroplatinate is at once precipitated as a deep brick-red powder, which, when washed with much cold water and dried, is pure. It is insoluble in hot water and has m. p. 203—204° (decomp.) (Found: C, 18·4; H, 3·3; N, 15·8. $C_{16}H_{36}N_{12}Cl_6S_4Co_2Pt$ requires C, 18·3; H, 3·5; N, 16·0%).

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, January 28th*, 1929.]

LX.—*Basic Chlorides and Addition Compounds from Metallic Chlorides and Hexamethylenetetramine. Exceptional Behaviour of Nickel Chloride.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

HEXAMETHYLENETETRAMINE is a weak base which can react with hot aqueous solutions of metallic chlorides to yield precipitates of basic chlorides. These precipitates in certain cases remain unchanged on prolonged heating with excess of the base. It seems probable,

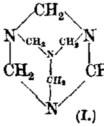
therefore, that the basic chlorides obtained in this way are definite compounds. The method described below is less likely to lead to the formation of mixtures than methods such as (1) the addition of regulated amounts of alkali in solution to solutions of normal salts, or (2) heating the solution of a normal salt with the corresponding oxide or hydroxide of the metal.

The formation of addition compounds between hexamethylenetetramine and metallic chlorides has also been investigated in order to extend the number of such compounds and to decide between discrepancies in the literature.

The Reactions of Metallic Chlorides with Hexamethylenetetramine in Boiling Aqueous Solution.—There was no evidence of change in the chlorides of magnesium, calcium, strontium, and barium when boiled in aqueous solution with hexamethylenetetramine. Zinc, ferric, chromic, aluminium, antimony, and tin chlorides all yielded the corresponding hydroxide; in the case of stannous chloride the precipitate of stannous hydroxide finally changed to black stannous oxide. From the chlorides of cadmium, lead, and bismuth were obtained the respective basic chlorides Cd(OH)Cl, Pb(OH)Cl, BiOCl.

The five metals which yielded results of most significance in this section were manganese, iron (ferrous), nickel, cobalt, and copper. It is to be noticed that these are placed consecutively in the periodic system. A basic chloride, $3M(OH)_2,MCl_2$ (M = Mn, Fe, Co, Cu), was obtained from the corresponding chloride MCl_2. In the case of nickel, such a basic chloride was not obtained, but the nature of the final product suggests that it had been formed as an intermediate compound. Basic chlorides of the above formulæ for manganese, cobalt, and copper have been obtained by other, but less definite methods. The ferrous compound, $3Fe(OH)_2,FeCl_2$, has not beer described previously: it is only stable in absence of air.

Nickel chloride behaves in an exceptional way, for (with th possible exception of lead) it afforded the only instance in which th basic chloride underwent further reaction with hexa methylenetetramine. The compound so obtaine is assigned the formula $N(CH_2{\cdot}OH)_3,3Ni(OH)_2$, bu its insoluble nature makes the determination c its constitution difficult. Probably, after som reaction between the basic chloride and the hexa methylenetetramine, the hexagon ring of the latt


(I.)

(I) is removed by hydrolysis as ammonia and formaldehyde, leavir the central part as $N(CH_2{\cdot}OH)_3$, which unites with the nick hydroxide:

$$C_6H_{12}N_4 + 6H_2O + 3Ni(OH)_2 \longrightarrow N(CH_2{\cdot}OH)_3,3Ni(OH)_2 + 3NH_3 + 3CH_2$$

Although trihydroxytrimethylamine has not been separated in the free state, several of its derivatives are known, *e.g.*, trimethylolamine sodium sulphite, $N(CH_2{\cdot}O{\cdot}SO_2Na)_3$, and tribenzamidotrimethylamine, $(C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2)_3N$; the latter compound was obtained by Descudé (*Compt. rend.*, 1902, **135**, 694) by heating benzamide with hexamethylenetetramine at 200°, and when boiled with dilute mineral acid yields benzamide, formaldehyde, and ammonia. The nickel compound decomposes in a similar manner, and when dried at 100° loses 3 molecules of water. It has not been found possible to obtain the compound in a state of purity by starting from nickelous hydroxide in place of the chloride, although partial formation was observed.

The behaviour of nickel compounds with amines in the presence of formaldehyde is being investigated.

Addition Compounds from Metallic Chlorides and Hexamethylenetetramine.—Rây and Sarkar (J., 1921, **119**, 390) gave a complete series of references to addition compounds of this type. Some of the formulæ recorded differ, principally as regards water of hydration, from those found by us (see Experimental). The formula $MCl_2,2C_6H_{12}N_4,10H_2O$ represents five addition compounds obtained in aqueous solution (M = Co, Ni, Mn, Mg, Ca). New addition *compounds* now described are $FeCl_2,2C_6H_{12}N_4,9H_2O$;

$SrCl_2,2C_6H_{12}N_4,9H_2O$; and $3ZnCl_2,2C_6H_{12}N_4,6H_2O$.

No addition compound of barium chloride could be separated. The cadmium chloride compound, $2CdCl_2,C_6H_{12}N_4,5H_2O$, has recently been described by Scagliarini and Brasi (*Atti R. Accad. Lincei*, 1928, [vi], **7**, 509). We had already prepared it in the course of this work.

Vanino and Schinner (*Arch. Pharm.*, 1914, **252**, 449—459) describe a cupric chloride compound, $2CuCl_2,C_6H_{12}N_4$, in which they did not determine chlorine; actually it is basic, with formula $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$. We have obtained a new cupric sulphate *compound*, $2CuSO_4,C_6H_{12}N_4,2H_2O$.

Reactions in Alcoholic Solution.—Metallic chlorides not stable in aqueous solution were found capable of yielding crystalline addition compounds with hexamethylenetetramine in alcoholic solution, and the following new *compounds* were thus prepared: $SnCl_2,2C_6H_{12}N_4$; $SnCl_4,4C_6H_{12}N_4$; $SbCl_3,3C_6H_{12}N_4$; $SbCl_5,6C_6H_{12}N_4$. These four have the same crystalline structure and their formulæ agree with those of corresponding addition compounds of the chlorides with ammonia. Bismuth chloride gave a crystalline *compound*, $BiCl_3,C_6H_{12}N_4$.

Where addition compounds can be prepared both in aqueous and in alcoholic solution, the proportions of hexamethylenetetramine in the pairs of compounds usually differ. We have obtained from alcoholic solution a new zinc chloride *compound*, $ZnCl_2,2C_6H_{12}N_4$.

EXPERIMENTAL.

Reactions between Metallic Chloride Solutions and Boiling Aqueous Hexamethylenetetramine Solutions.

Method.—To a 20% aqueous solution of hexamethylenetetramine (3 mols.) boiling under reflux, a 15% (or saturated, if below this strength) solution of the metallic chloride (1 mol.) was gradually added, and boiling was continued for at least an hour. The solution was then cooled and filtered, and the precipitate washed with water. Modifications which were necessary in certain cases are indicated below. Hexamethylenetetramine was usually estimated by hydrolysis to ammonium salt with hydrochloric acid and distillation of the ammonia into standard acid. Wherever possible, the result was checked by hydrolysing the substance with acid under reflux and adding excess of standard iodine, followed by excess of sodium hydroxide; after 30 minutes, the solution was acidified, and the excess of iodine determined by thiosulphate titration. This method determined the formaldehyde, from which the amount of hexamethylenetetramine could be calculated. The two methods together thus checked the possibility of any breaking down of the molecule of the base before uniting with the metallic chloride or its hydroxide. This applies particularly to the case of nickel (see below). The following definite results were obtained in this section.

1. Magnesium chloride gave no basic precipitate. When the solution was cooled, large, colourless, flat needles were obtained and identified as bishexamethylenetetramine magnesium chloride decahydrate, $MgCl_2,2C_6H_{12}N_4,10H_2O$ (Found: Mg, 4·27; Cl, 12·53; $C_6H_{12}N_4$, 49·5; H_2O, 31·4. Calc.: Mg, 4·38; Cl, 12·80; $C_6H_{12}N_4$, 50·4; H_2O, 32·4%). This compound is the same as that formed when cold concentrated solutions of the two components are mixed.

2. Zinc, ferric, aluminium, and chromic chlorides gave the corresponding hydroxides. Stannous chloride gave first stannous hydroxide, which later changed on continued boiling to black glistening plates of stannous oxide.

3. Bismuth chloride, dissolved in the minimum amount of hydrochloric acid, yielded a white precipitate of the oxychloride, BiOCl (Found: Cl, 13·42. Calc.: Cl, 13·68%). There was no change on prolonged boiling except above the surface of the liquid, where any white precipitate on the glass became black through the reducing action of formaldehyde vapour and ammonia arising from decomposition of hexamethylenetetramine.

4. Mercuric chloride gave mercury as a final product. A basic yellow precipitate of varying composition was first formed; it was unchanged in the dark but turned grey on exposure to sunlight.

5. Cadmium chloride yielded a white precipitate of the basic salt Cd(OH)Cl (Found: Cd, 68·1, 68·2; Cl, 21·3, 21·4. Calc.: Cd, 68·2; Cl, 21·5%).

6. Lead chloride yielded a white precipitate of basic lead chloride, Pb(OH)Cl (Found: Pb, 79·4; Cl, 13·6. Calc.: Pb, 79·6; Cl, 13·7%). On prolonged boiling, the precipitate turned brown, losing its chlorine and becoming an amorphous product containing complex organic matter. The solution also turned dark brown, and when evaporated became a thick treacle-like syrup.

7. Cupric chloride yielded a pale blue precipitate of basic cupric chloride, $3Cu(OH)_2,CuCl_2$ (Found: Cu, 59·1; Cl, 16·9. Calc.: Cu, 59·5; Cl, 16·6%).

8. Cobaltous chloride yielded a pink precipitate of basic cobaltous chloride, $3Co(OH)_2,CoCl_2$ (Found: Co, 57·4; Cl, 17·2. Calc.: Co, 57·7; Cl, 17·4%).

9. Manganese chloride gave a definite result when air was excluded and more concentrated solutions were used. The white precipitate obtained was identified as the basic chloride, $3Mn(OH)_2,MnCl_2$ (Found: Mn, 55·5; Cl, 17·8. Calc.: Mn, 55·9; Cl, 18·1%); it became brown in air. From the hot filtrate there were obtained pale pink crystals of *the addition compound*, $MnCl_2,2C_6H_{12}N_4,10H_2O$ (Found: Mn, 9·4; Cl, 12·1. Calc.: Mn, 9·4; Cl, 12·1%).

10. Ferrous chloride yielded a white precipitate of *basic ferrous chloride*. The preparation was made in a hydrogen atmosphere, and the precipitate protected by hydrogen during filtration and washing [Found: Fe, 56·7; Cl, 16·9. $3Fe(OH)_2,FeCl_2$ requires Fe, 58·9; Cl, 17·9%]. The compound readily became brown in air. For a more accurate check on the proportions of iron and chlorine, freshly precipitated samples were washed and at once dissolved in dilute sulphuric acid; two determinations with different samples then gave Cl : Fe = 1 : 2·020 and 1 : 2·024.

11. The precipitate formed on adding nickel chloride solution to a boiling aqueous solution of hexamethylenetetramine always contained some portion of the base. Even after 30 minutes' boiling, the precipitate had a chlorine content of about 5%, and ammonia and formaldehyde could be obtained from it on decomposition. A definite compound was finally obtained by boiling the precipitate for about 8 hours, the solution being changed for fresh solution of hexamethylenetetramine three times, until the precipitate was free from chloride. A pale green sandy powder was obtained and identified as an addition *compound* of nickel hydroxide and trihydroxytrimethylamine [Found: Ni, 45·7, 45·7; N, 3·4, 3·6; CH_2O, 23·3, 23·4. $N(CH_2{\cdot}OH)_3,3Ni(OH)_2$ requires Ni, 45·7; N, 3·6; CH_2O, 23·4%]. The nitrogen was estimated as ammonia and

the CH_2O group as formaldehyde. The compound loses 15·0% of water at 95° (Calc. for $3H_2O$: 14·02%) without marked change in colour or in chemical nature. It is odourless and insoluble in water. It differs from nickel hydroxide in being insoluble in boiling formaldehyde solution. There is no reaction with boiling sodium hydroxide solution, and attempts to reduce the compound with sodium and alcohol and with sodium hydrosulphite failed. When left over-night in cold *N*-hydrochloric acid solution, very little dissolves, but the residue on drying contains chloride and smells of formaldehyde. The compound is decomposed on boiling with dilute mineral acid, yielding ammonia, formaldehyde, and a nickel salt. A suspension of the compound in water is decomposed by hydrogen sulphide, yielding an aqueous solution of ammonium sulphide and an insoluble grey product having the unpleasant odour of polymerised thioformaldehyde and containing nickel sulphide. The probable reaction is $N(CH_2{\cdot}OH)_3,3Ni(OH)_2 + 7H_2S = NH_4HS + 3NiS + 3CH_2S + 9H_2O$. Freshly precipitated nickel hydroxide was boiled with excess of 20% aqueous hexamethylenetetramine solution for 6 hours. Analysis of the resulting insoluble green product (Found : N, 1·28; CH_2O, 8·35%; N : CH_2O = 1 : 3·03) showed that partial formation of the above addition compound had resulted. Complete conversion was not expected because of the insoluble gelatinous nature of nickel hydroxide. This supports the view that the addition compound described above is derived from a basic nickel chloride, probably $3Ni(OH)_2,NiCl_2$, formed as an intermediate product from nickel chloride.

Addition Compounds in Alcoholic Solution.

Method.—Cold solutions of the chlorides in absolute alcohol were added gradually with constant stirring to excess of hexamethylenetetramine dissolved in absolute alcohol. The crystalline compounds separated immediately and were at once collected and washed with absolute alcohol. The four tin and antimony compounds all formed colourless, microscopic, oblong plates. The following compounds were thus obtained.

1. *Bishexamethylenetetramine stannous chloride* (Found : Sn, 25·04; Cl, 15·17; $C_6H_{12}N_4$, 58·53. $SnCl_2,2C_6H_{12}N_4$ requires Sn, 25·27; Cl, 15·12; $C_6H_{12}N_4$, 59·60%). When heated, this compound chars extensively, giving ammonia and formaldehyde, and leaving a residue of tin; it is decomposed by cold water, with formation of stannous hydroxide.

2. *Tetrakishexamethylenetetramine stannic chloride* (Found : Sn, 14·4; Cl, 17·2; $C_6H_{12}N_4$, 67·3. $SnCl_4,4C_6H_{12}N_4$ requires Sn, 14·5; Cl, 17·3; $C_6H_{12}N_4$, 68·2%). When heated, this compound behaves

like the stannous chloride compound; with water it is hydrolysed to α-stannic acid.

3. *Trishexamethylenetetramine antimony trichloride* (Found: Sb, 18·6; Cl, 16·5; $C_6H_{12}N_4$, 63·9. $SbCl_3,3C_6H_{12}N_4$ requires Sb, 18·6; Cl, 16·5; $C_6H_{12}N_4$, 5·0%) decomposes in water to give antimony hydroxide, $Sb(OH)_3$ (Found: Sb, 71·0. Calc.: Sb, 70·2%).

4. *Hexakishexamethylenetetramine antimony pentachloride* (Found: Sb, 10·15; Cl, 15·2; $C_6H_{12}N_4$, 72·9. $SbCl_5,6C_6H_{12}N_4$ requires Sb, 10·55; Cl, 15·6; $C_6H_{12}N_4$, 73·8%) decomposes in water but not completely until the mixture is heated, whereupon antimonic acid, $HSbO_3$, is obtained (Found: Sb, 71·1. Calc.: Sb, 71·0%). Although much formaldehyde is produced on boiling antimony pentachloride with aqueous hexamethylenetetramine solution, there is no noticeable reduction to antimonous compound.

5. *Hexamethylenetetramine bismuth trichloride* was obtained as white microscopic crystals (Found: Bi, 45·4; Cl, 22·9; $C_6H_{12}N_4$, 31·4. $BiCl_3,C_6H_{12}N_4$ requires Bi, 45·8; Cl, 23·4; $C_6H_{12}N_4$, 30·8%). This compound was decomposed by water to bismuth oxychloride, BiOCl (Found: Cl, 13·52. Calc.: Cl, 13·68%).

6. *Bishexamethylenetetramine zinc chloride* separated as a very voluminous, white, microcrystalline powder (Found: Zn, 15·9; Cl, 17·3; $C_6H_{12}N_4$, 66·5. $ZnCl_2,2C_6H_{12}N_4$ requires Zn, 15·7; Cl, 17·05; $C_6H_{12}N_4$, 67·2%); unlike the compound prepared from aqueous solutions (p. 418), this dissolves readily in water, but on standing, slowly deposits zinc hydroxide.

Addition Compounds prepared in Aqueous Solution.

Method.—A concentrated aqueous solution of the chloride was stirred into excess of a concentrated aqueous solution of hexamethylenetetramine. This yielded crystalline precipitates immediately for the cadmium, zinc, and calcium compounds, but evaporation was necessary to obtain the strontium compound. Air was excluded by hydrogen in the preparation of the ferrous compound. All the precipitates were washed finally with alcohol. The estimation of the hexamethylenetetramine portion of the compounds was made by the methods indicated on p. 414. Water of crystallisation was determined where possible at 95°.

1. Hexamethylenetetramine di-cadmium chloride pentahydrate, $2CdCl_2,C_6H_{12}N_4,5H_2O$, was obtained as a white microcrystalline powder (Found: Cd, 37·2, 37·1; Cl, 23·7, 24·0; $C_6H_{12}N_4$, 23·7, 23·5; H_2O, 14·0, 14·1. Calc.: Cd, 37·7; Cl, 23·8; $C_6H_{12}N_4$, 23·5; H_2O, 15·1%). When stirred in *N*-hydrochloric acid it dissolved, and the colourless needles which separated were identified as $CdCl_2,C_6H_{12}N_4,HCl,H_2O$ (Found: Cd, 29·4; Cl, 28·1; $C_6H_{12}N_4$,

37·7. Calc.: Cd, 29·7; Cl, 28·2; $C_6H_{12}N_4$, 37·0%), which had previously been obtained from hydrochloric acid solutions of the chloride and the base.

2. *Bishexamethylenetetramine tri-zinc chloride hexahydrate* was obtained as a white microcrystalline powder (Found: Zn, 24·8; Cl, 25·9; $C_6H_{12}N_4$, 35·0. $3ZnCl_2,2C_6H_{12}N_4,6H_2O$ requires Zn, 24·7; Cl, 26·7; $C_6H_{12}N_4$, 35·1%). When stirred with water it is hydrolysed to basic zinc chloride of indefinite composition.

3. *Bishexamethylenetetramine calcium chloride decahydrate* was obtained in minute colourless crystals (Found: Ca, 7·1; Cl, 12·5, 12·4; $C_6H_{12}N_4$, 49·15, 48·5; H_2O, 30·9. $CaCl_2,2C_6H_{12}N_4,10H_2O$ requires Ca, 7·0; Cl, 12·4; $C_6H_{12}N_4$, 49·0; H_2O, 31·5%). The compound is not deliquescent. It can be boiled in solution and recovered unchanged. We have prepared it both from cold solutions and by mixing boiling solutions of the components, but it has always separated as a decahydrate: we have been unable to prepare the hexahydrate which Vanino and Schinner (*loc. cit.*) describe.

4. *Bishexamethylenetetramine strontium chloride nonahydrate*, obtained in colourless minute crystals like those of the calcium compound (Found: Sr, 14·75; Cl, 11·9, 11·8; $C_6H_{12}N_4$, 46·6, 46·9; H_2O, 26·5. $SrCl_2,2C_6H_{12}N_4,9H_2O$ requires Sr, 14·6; Cl, 11·8; $C_6H_{12}N_4$, 46·6; H_2O, 27·0%), is stable in boiling water.

5. *Bishexamethylenetetramine ferrous chloride nonahydrate*, $FeCl_2,2C_6H_{12}N_4,9H_2O$, was obtained as very pale green microscopic plates when a fresh solution of ferrous chloride (made from iron and concentrated hydrochloric acid) was run into cold concentrated aqueous hexamethylenetetramine solution in an atmosphere of hydrogen. The crystals were washed with alcohol and then ether, pressed between filter paper, and at once analysed (Found: Fe, 10·1; Cl, 12·7; $C_6H_{12}N_4$, 48·4; H_2O, 28·9. $FeCl_2,2C_6H_{12}N_4,9H_2O$ requires Fe, 9·8; Cl, 12·5; $C_6H_{12}N_4$, 49·2; H_2O, 28·5%). The compound is not stable in air, becoming brown through oxidation; even in a closed tube it becomes brown and wet from its own water content.

6. *Basic hexamethylenetetramine cupric chloride dihydrate*, $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$. We have not been able to obtain the compound $2CuCl_2,C_6H_{12}N_4$ described by Vanino and Schinner (*loc. cit.*). In attempts to avoid formation of a basic compound, the following method was tried: Saturated aqueous cupric chloride solution was added drop by drop and with vigorous shaking to excess of hexamethylenetetramine in alcoholic solution. The brown precipitate obtained was not apparently crystalline [Found, for two preparations: Cu, 29·3, 30·2; Cl, 24·4, 24·3; $C_6H_{12}N_4$, 31·[illegible] 31·3. $Cu(OH)Cl,CuCl_2,C_6H_{12}N_4,2H_2O$ requires Cu, 29·8; Cl, 24·9[illegible]; $C_6H_{12}N_4$, 32·8%.] Vanino and Schinner gave no figures for chlori[illegible]

in their compound. When the brown compound was stirred in water it gave immediately the pale blue basic cupric chloride $3Cu(OH)_2,CuCl_2$ (Found: Cu, 58·87; Cl, 16·37. Calc.: Cu, 59·54; Cl, 16·61%).

7. *Hexamethylenetetramine di-cupric sulphate dihydrate* was obtained in grass-green microscopic crystals when concentrated aqueous cupric sulphate solution was added in drops to alcoholic hexamethylenetetramine solution (Found: Cu, 25·7; SO_4, 38·8; $C_6H_{12}N_4$, 27·2; H_2O, 7·0. $2CuSO_4,C_6H_{12}N_4,2H_2O$ requires Cu, 25·7; SO_4, 38·8; $C_6H_{12}N_4$, 28·3; H_2O, 7·3%); it decomposed in water, yielding pale blue basic cupric sulphate, $3Cu(OH)_2,CuSO_4$ (Found: Cu, 56·50; SO_4, 21·47. Calc.: Cu, 56·23; SO_4, 21·22%).

8. Hexamethylenetetramine di-cupric acetate was obtained as dark green microscopic needles on mixing concentrated aqueous cupric acetate solution with excess of alcoholic hexamethylenetetramine solution [Found: Cu, 25·2; OAc, 46·1; $C_6H_{12}N_4$, 28·0. Calc. for $2(CH_3·CO_2)_2Cu,C_6H_{12}N_4$: Cu, 25·3; OAc, 46·9; $C_6H_{12}N_4$, 27·8%]. Vanino and Schinner (*loc. cit.*) prepared this compound, but used cupric chloride solution, acetic acid, and hexamethylenetetramine in aqueous solution.

CENTRAL TECHNICAL COLLEGE,
BIRMINGHAM. [*Received, December 8th*, 1928.]

LXI.—*The Decomposition of Methane. Part I.*

By CYRIL WILLIAM HART JONES.

THE object of the present work is to investigate (*a*) the thermal decomposition of methane under various conditions of temperature, pressure, and times of heating and (*b*) the behaviour of the gas when subjected to the action of the electric spark.

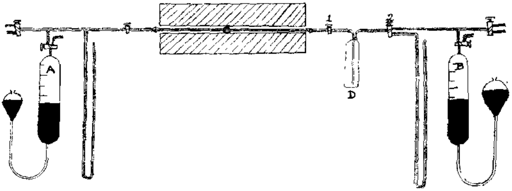
The methane used was natural gas from a South Wales colliery. It contained 92·5% of methane, 3·5% of hydrogen, and 3·9% of nitrogen. Analyses were carried out in a Bone and Wheeler apparatus, following the scheme of Williams-Gardner (*Fuel*, 1925, 4, 430).

A. Thermal Decomposition of Methane.

The apparatus is shown diagrammatically in Fig. 1. The dried methane from the cylinder was introduced to the graduated gas holder, A. The apparatus was exhausted and the gas passed at the desired pressure and rate of flow to the gas holder, B, through the heated quartz capillary tube, C. This tube, of 1 mm. internal diameter and 2 mm. wall thickness, was 120 cm. long, and a length of

80 cm. was heated to a constant temperature by means of an electric tube furnace. D is a condenser cooled in a mixture of acetone and solid carbon dioxide. After passage of the gas, the apparatus was exhausted, tap 1 closed, and tap 2 opened to the manometer. The condenser was allowed to attain room temperature, and thus the presence of easily condensable hydrocarbons was indicated, whilst oil or solid matter could be seen on the walls of the condenser. After each experiment a stream of oxygen was passed through the heated quartz tube to burn out any carbon formed, so that the internal surface of the tube was the same at the beginning of each experiment.

FIG. 1.



Results.—In the first series of experiments the gas was passed at constant pressure between the gas holders ten or twelve times, the percentage increase in pressure at constant volume being noted after each passage. Samples of the gas taken after such treatment showed the only decomposition products to be carbon and hydrogen, the former forming a hard, lustrous, coherent coating on the walls of the quartz tube. The temperature range investigated was 700—1080°, and the rates of flow were 100, 200, or 300 cm. per sec. The pressures were between 10 and 70 cm. of mercury. At 700° the increase in pressure was very small, at 800° and a rate of flow of 200 cm. per sec. the increase after ten passages through the tube was 2·5%, whilst at 1080° and a rate of 100 cm. per sec. it was 32·0% for the same number of passages. For intermediate temperatures the increase lay between these values, being lower at greater rates of flow. The increase in pressure was greater during the earlier passages through the tube than during the later ones.

In the second series of experiments the gas was passed only once through the tube under similar conditions of temperature and pressure to the above. In no case did more than 5% of the methane decompose, and, as judged from the amount of hydrogen present in the heated gas, this decomposition was almost entirely into carbon and hydrogen. At 800° and 900° traces of olefinic hydrocarbons

were formed, but the amounts were too small to admit of accurate determination. At 1000° appreciable amounts were formed, as shown in Table I, which shows the relation between the pressure of gas during the heating and the proportion of olefins for two different rates of flow. At 300 cm./sec. the proportions were smaller and the results less trustworthy.

TABLE I.

Gas pressure, cm.	10	20	30	40	50	60	70
Olefins, %, at 100 cm./sec.	0·13	0·78	1·25	1·55	1·75	1·61	0·84
,, ,, 200 ,,	Trace	0·27	0·49	0·38	0·16	0·15	Trace

Small amounts of acetylene were formed at all temperatures and pressures, the maximum yield occurring at a pressure of 30—40 cm. Easily condensable hydrocarbons were not formed under the experimental conditions.

The work is being continued at the same and higher temperatures and at the same and lower flow speeds, and a much improved apparatus is being constructed.

B. The Sparking of Methane.

The apparatus consisted of an explosion pipette of about 200 c.c. capacity, fitted with platinum wire electrodes and connected to a constant-volume manometer. After having its pressnre measured in the manometer, a quantity of methane was passed into the pipette and brought to the desired pressure. The spark was passed intermittently in order to avoid overheating the electrodes, the pressure of the gas being kept constant. The pressure of the gas at constant volume was measured at frequent intervals and samples were drawn off and analysed; the pressure was found to rise in accordance with the values shown in Table II. The influence of pressure on the course of the reaction is noteworthy, decomposition being much faster at higher concentrations.

TABLE II.

Time of sparking (mins.).	Percentage increase in pressure at given pressures (cm.) during sparking.						
	10.	20.	30.	40.	50.	60.	70.
1	5·5	13·0	17·25	22·5	21·0	28·0	28·5
2	10·5	22·5	30·0	37·0	35·0	46·0	47·0
3	15·5	30·0	39·0	47·0	46·0	60·0	62·0
4	20·0	35·5	46·0	56·0	58·0	71·0	74·0
5	23·5	41·5	52·5	63·0	63·5	79·5	81·5
6	27·0	47·0	57·5	70·0	72·0	85·0	87·5
7	30·0	51·5	61·5	73·5	77·0	88·5	90·5
8	33·0	58·0	61·5	77·0	—	92·0	93·5
9	36·0	58·0	69·5	80·0	—	—	—
10	37·5	61·8	71·0	81·5	—	—	—

From these figures it may be calculated that the reaction is mainly bimolecular, but tends to become more complex as the decomposition proceeds. Analysis of the sparked gas showed the main reaction to be direct decomposition to carbon and hydrogen, but high percentages of olefinic and acetylenic hydrocarbons are formed, as shown in Table III.

TABLE III.

Time of sparking (mins.).	Olefins, %, at stated pressures.			Acetylenes, %, at stated pressures.		
	40 cm.	60 cm.	70 cm.	40 cm.	60 cm.	70 cm.
1	1·10	2·05	3·90	7·50	4·85	5·20
2	1·55	3·15	5·35	8·45	7·40	7·75
3	1·90	3·70	5·90	8·90	7·55	7·80
4	2·20	4·05	6·00	9·00	7·00	7·85

The formation of both olefins and acetylenes is very rapid at first, but there is a tendency for the percentage of these components to reach a steady level. The yield of olefins appears to be roughly proportional to the pressure of the gas during sparking, but the highest yield of acetylenes is obtained at about ½ atmosphere.

Small amounts of complex solid and liquid hydrocarbons were formed on the walls of the pipette. The carbon produced by direct decomposition of the gas to its elements tended to form a bridge across the spark gap.

Summary.

1. The decomposition of methane when passed through a heated quartz tube is chiefly into its elements. Small amounts of olefinic and acetylenic hydrocarbons are also formed.

2. When methane is subjected to the electric spark discharge, carbon, hydrogen, olefins, and acetylenes are formed, together with small quantities of higher unsaturated hydrocarbons.

In conclusion, my best thanks are due to Professor F. G. Donnan, F.R.S., who suggested and supervised the work, and to the Department of Scientific and Industrial Research for a grant which enabled it to be carried out.

THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, November 22nd*, 1928.]

LXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXX. The Nitration of Phenylbromocyanonitromethane, with Special Reference to an Alleged Example of Intramolecular* meta-*Rearrangement.*

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

THE important part played by the nitration of phenylbromocyano-itromethane in the history of the theory of aromatic substitution ed us to reinvestigate this reaction, with the result (J., 1926, 462) that we had to controvert Flürscheim's original statement *J. pr. Chem.*, 1902, **66**, 328) that the *p*-nitro-derivative alone is ormed. Flürscheim and Holmes subsequently published (J., 1928, 53) a detailed examination of the reaction, and, whilst con-irming our finding to the extent of showing that the principal roduct of nitration is the *m*-derivative (thus bringing this case nto line with phenylnitromethane itself, and with β-phenyl-β-nitro-ropane and other derivatives of the form $C_6H_5{\cdot}CR_2{\cdot}NO_2$, all of hich we had shown to yield large proportions of *m*-compound), ivestigated also a number of side reactions leading to products hich when oxidised gave *p*-nitro- and *m*-bromo-benzoic acids. hese side reactions (lateral decomposition) form the main subject f the present paper.

(A) *Conditions of Occurrence of the Side Reactions.*

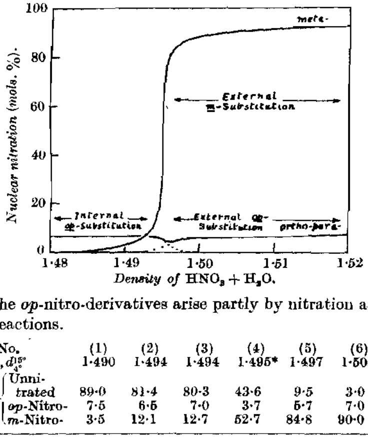
Since water, although it facilitates the ionisation $H^{\cdot}(O{\cdot}NO_2)'$, ill oppose any tendency towards $(OH)'(NO_2)^{\cdot}$, nitration velocities ust in general be strongly dependent on the water content of he nitric acid. It is consistent that the most important factor etermining the conditions under which lateral decomposition ends to replace the normal (mainly *meta*) nitration of phenyl-romocyanonitromethane is the concentration of the nitric acid. n order to indicate the magnitude and limits of this effect we ave carried out a series of nitration experiments under identical onditions, namely, those previously employed, but with acid arying in strength from $d_4^{15°}$ 1·490 to $d_4^{15°}$ 1·517 (see E,* 2, *a*). The gures, which appear consistent with those published by Flürscheim nd Holmes only in the regions where the result is relatively little ependent on the strength of the acid,† are in the first table, from

* Throughout, E refers to the experimental section.

† When phenylnitromethane is treated for 3 hours at −15° to 0° with itric acid, *d* 1·52 (10 parts), mononitration proceeds without the formation f by-products. With acid, $d_4^{15°}$ 1·482, under conditions otherwise the same,

which Fig. 1 is plotted. The second table, which refers to nitration under other conditions (see E, 2, *b*), shows that the speed of the side reactions, unlike that of nitration, is comparatively slightly affected by the strength of the acid, at least within considerable limits; for longer contact with a weaker acid increases lateral decomposition (as measured by brominated products), but decreases direct nitration (as measured by meta-nitration) despite the increased

FIG. 1.



time. The *op*-nitro-derivatives arise partly by nitration and partly by side reactions.

Nitration No.		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Nitric acid, $d_{4°}^{15°}$		1·490	1·494	1·494	1·495*	1·497	1·505	1·517
Acids by $KMnO_4$ oxidation (%).	Unnitrated	89·0	81·4	80·3	43·6	9·5	3·0	1·5
	op-Nitro-	7·5	6·5	7·0	3·7	5·7	7·0	6·2
	m-Nitro-	3·5	12·1	12·7	52·7	84·8	90·0	92·3

nitration is not quantitative, but the proportion of *m*-derivative in the nitro phenylnitromethanes is the same as before, namely, 66·8 ± 1·0%, which figur should therefore replace the lower one given by us previously.

* This is the acid used by us formerly, the density of which was given i the uncorrected form *d* 1·49, as we were not then aware of the importanc of the fourth figure. Flürscheim and Holmes, although aware of the notab influence of small density differences, stated that *m*-nitration does not occu appreciably under our conditions, but it will be seen that we have confirme our previous estimate of the *m*-content almost exactly. Furthermore, the attribute to us a statement that the small amount of *p*-nitrobenzoic acid the oxidation acids is not accompanied by a larger amount of benzoic aci but we cannot find any such assertion: the only statement bearing on t point is that benzoic acid is present, and in quantity sufficient for isolatio Again, they refer to the ultimate analysis of the oxidation acids as provi the statement they attribute to us; but the conclusion is theirs, and unjustified, if for no other reason than that the mixtures contain bromo-aci

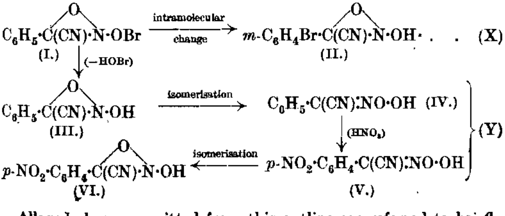
No.	HNO_3 $d_{4°}^{15°}$.	Time (days).	Acids by $KMnO_4$-oxidation (mols. %). Unsubstituted.	Bromo-.	*op*-Nitro-.	*m*-Nitro-.
8	1·482	10	0·0	38·1	20·1	41·8
{ 9	1·455	14	34·5	48·5	9·0	8·0
{ 10	1·455	33	4·6	59·1	22·6	13·6

The lateral decomposition takes place also in the absence of nitric acid (E, 10, 11, and 12), and the significance of this is discussed later (C, 1 and 2).

(B) *Nature of the Side Reactions. Section (i). A Criticism.*

(1) *Summary of Flürscheim and Holmes's Conclusions.*—The remarkable conclusions of these authors may be summarised by the statement that the process of lateral decomposition which leads, after oxidation, to *m*-bromobenzoic acid is an *intramolecular* *m*-migration of bromine, to be formulated * as at (X), whereas that which leads, after oxidation, to *p*-nitrobenzoic acid is dependent on an *extramolecular* *p*-nitration of the nucleus, and is to be represented as at (Y).

The following changes are stated to take place, in addition to the *m*-migration leading to (II), namely, reduction of the original substance (I), re-arrangement of the reduction product (III), nitration of the isomeride (IV) thus formed, and conversion of the nitration product (V) into its isomeride (VI) :



Alleged changes omitted from this outline are referred to briefly under (B, 4).

(2) *Formation of* m-*Bromo-derivatives.*—Flürscheim and Holmes regard process (X) as " the first proved case of *intramolecular*

* The reproduction in this section of Flürscheim and Holmes's cyclic formulæ is for accuracy in quotation, and does not imply our acceptance of their arguments in favour of this method of formulation. For a discussion of the significance of " hypobromite reactions " in *C*- and *O*-halogen compounds, see Ingold and Shoppee, J., 1928, 382—383.

m-migration" of a substituent in a side chain.* Furthermore, taking it together with the "almost exclusive extramolecular *m*-nitration of phenylbromocyanonitromethane," they state that it "proves that the law governing direct and indirect *m*-substitution is the same—just as the same law has long been known to apply to direct and indirect substitution in the *o*- and *p*-positions." This *m*-migration from a *m*-orienting side chain is stated to agree with their "theory of affinity distribution."

We think we understand how a theory, which, for a *m*-orienting benzene derivative, C_6H_5·R, postulates a distribution giving an enhanced affinity-field to the *m*-position, can accommodate *m*-migration arising from the attraction by the enhanced meta-field of some loosely bound portion of R. We are, however, prepared *to say that such an occurrence is scarcely possible* on our theory, according to which the meta-field (electrostatic) is *permanently reduced by* R (— *I* effect), without the possibility of relief from those momentary excitations (*T* effect) which may make the (normally also de-activated) *op*-positions the centres of instantaneous attracting fields extending to the side chain (compare Ingold and Shaw, J., 1927, 2918). Our view is, in short, that if any portion of R migrates internally to the nucleus it should reach the *op*-positions, never the *m*-position; that the chances of its reaching the *m*-position should be smaller the stronger the *m*-orienting power of R; and that there should be no common law applying to direct and to indirect *m*-substitution. We were accordingly disposed to question this "first proved case," despite the definite character of Flürscheim and Holmes's statements with regard to the evidence.

Three reasons are given for regarding the transference of bromine as taking place by an intramolecular process. Of these, the first two are the "observations" (*a*) that the progress of the reaction is "not affected by the addition of a substance containing a *m*-directing group," and (*b*) that the rate of migration of bromine is "independent of the concentration." Our experiments do not enable us to confirm either statement. As to (*a*), we find that the addition of a second substance containing a *m*-directing group *causes a large proportion* (*e.g.*, about 40%) *of the bromine to be transferred to the* m-*position of that substance* (see E, 4).

Argument (*b*) would not in any case be cogent, because the invariance of the rate, even if established, would be capable of several explanations (as that it is determined by a pseudo-unimolecular change to a more rapidly brominated product, or that the brominating agent is volatile and that the medium becomes satu

ated with it, etc.). Our experiments show (1) that the dynamics of the bromine transference are far from simple; for example, there is almost certainly a period of induction (see E, 5). Furthermore, we find (2) that factors foreign to homogeneous reaction-dynamics, such as the escape of gases from the reaction mixture, influence the accumulation of nuclear bromine (see E, 8). In the circumstances *it is difficult to attach a definite numerical significance* to the term "rate," and the translation of yields into rates is challengeable; nevertheless, we find (3) that the yields obtained after equal times at different concentrations are, contrary to the indications of Flürscheim and Holmes, so widely different as to show that their simple view of the dynamics of the process is far from adequate (see E, 3). The observations summarised under (1) and (2) above will be referred to again later; those summarised under (3) may be illustrated here by the following table, in which the brackets indicate groups of experiments in which all conditions were identical excepting the initial concentration of phenylbromocyanonitromethane (PBCN).

	(E, 3, *a*; 20 hours' nitration).				(E, 3, *b*; 240 hours' nitration).		
Nitration No.	11	12	13	14	15	16	17
Conc. PBCN, wt. %	100·0	66·7	33·3	9·1	11·1	5·9	4·0
m-Bromo-, mols. %	1·2	8·6	19·9	37·2	49·0	38·1	29·2

We have no doubt that the relationship here exhibited is part of a much more complicated connexion between the concentration and the rate of transference of bromine to the nucleus; it is obvious, nevertheless, that the rate is not *independent* of the concentration.

The remaining argument (*c*) is that the presence of the product (II) to be expected from the intramolecular rearrangement (X) has been "conclusively established." We think, however, that this statement is exaggerated. The reason for it is that, *in Flürscheim and Holmes's opinion*, *m*-bromophenylbromocyanonitromethane, which *is* present, is formed from (II) by the action of hypobromous acid, which they consider to be produced as shown at (Y), and to be present in quantities sufficient for detection in the spent nitric acid solutions. We shall show below that hypobromous acid is absent (see B, 4 and E, 5), and that there is a simpler explanation of the formation of *m*-bromophenylbromocyanonitromethane (compare C, 1).

Summarising our experiments, it appears that none of the reasons given by Flürscheim and Holmes for regarding the bromine-transference as intramolecular survives experimental re-examination; nor is there at present any proof that the initial product of such a change is formed at all.

(3) *Formation of* p-*Nitro-derivatives.*—The only direct argument advanced by Flürscheim and Holmes in support of their claim to have "quantitatively elucidated" the group of reactions (Y) is the statement that they have "conclusively established" the presence of two of the postulated compounds, namely (III) and (VI).

The presence of (III) is inferred from the presence amongst the products of a phenyl derivative which, when directly boiled with permanganate, gives *p*-nitrobenzoic acid and an excess of benzoic acid. This effect is *assumed* to be due to the decomposition of (III); but there is no other evidence that (III) is actually the substance responsible, and the same assumption might equally have been made with regard to any other hypothetical intermediate (still containing side-chain nitroxyl) possibly present during permanganate oxidation. We have, however, prepared (III) and find that it decomposes *by itself* with a considerable transference (more than 20%) of the nitro-group from the side chain to the *p*-position (see E, 13); so that even if the existence of (III) in the nitration solution were established (which is not yet the case) the fact would tell against, and not in favour of, the theory that the few units % of *p*-nitro-products formed by lateral decomposition arise from extramolecular nitration of the aromatic nucleus by nitric acid (compare C, 2).

Flürscheim and Holmes's "proof" that (VI) is present rests *on their statement that p-nitrophenylbromocyanonitromethane is* present in substantial excess of the quantity attributable to direct nitration of phenylbromocyanonitromethane, together with their opinion that this excess arises by the action of hypobromous acid (which, in reality, is absent) on (VI). Flürscheim and Holmes record, for instance, that the *op*-nitrophenylbromocyanonitromethanes formed on nitration with nitric acid $d_{4^\circ}^{15^\circ}$ 1·480 amount to about 60% of the quantity of *m*-isomeride; and they attribute the excess (presumably over about the first 10%) to the action of hypobromous acid on the hypothetical intermediate (VI). We have carefully examined this matter, both by following Flürscheim and Holmes's experimental method for the estimation of the *op* and *m*-compounds, and also by a more direct method. By both methods we find (see E, 9) that the quantity of *op*-nitrophenylbromocyanonitromethanes formed by acid of the strength given constitutes only about 10% of the nitro-derivatives possessing an unaltered side chain; and this is approximately the quantity which might be expected to arise by direct nitration of phenylbromocyanonitromethane.

We are therefore unable to agree with any of the evidence

advanced by Flürscheim and Holmes in favour of their theory of external nuclear nitration, and in the sequel we shall propose an alternative theory (C, 2 and D, 3).

(4) *Additional Details.*—The remaining reactions which Flürscheim and Holmes claim to have elucidated are contained in their paper in three somewhat elaborate schemes (*loc. cit.*, pp. 457, 458, 460), none of which requires further consideration, since each is fundamentally dependent on one or more of the points already discussed. The following matter is, however, of some importance.

Flürscheim and Holmes postulate the intervention of hypobromous acid and consider this substance to be present in the nitration solution in quantity corresponding to the production of a " very material precipitation of silver bromide "; it is stated, moreover, that the conditions of their tests were such as to indicate the practical absence of free bromine from their solutions. Contrary to both these statements, we have (*a*) been unable to convince ourselves of the presence of *any* hypobromous acid (see E, 5), and (*b*) have established the presence of a *large amount* of free bromine (see E, 6). The reliability of our negative result (*a*) is indirectly confirmed by the positive result (*b*) (compare also *c*, below) for the following reason. The equilibrium ratio $[H^{\cdot}][Br'][HOBr]/[Br_2]$ is known (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 938) to be of the order of 10^{-8}; it is also known that this equilibrium is established very rapidly. Therefore, even in a comparatively dilute acid solution, containing no *extraneous* bromide ions, the concentration of hypobromous acid could be only an almost infinitesimal fraction of that of the bromine; actually the solutions are strongly acid, which makes the fraction much smaller still. This conclusion is additionally enforced by our further observation (*c*) that a comparatively large amount of extraneous bromide ion in the form of free hydrobromic acid is present (see E, 6). This must further reduce the concentration of hypobromous acid to a minute fraction of the already infinitesimal trace which might have existed in its absence. Therefore, known thermodynamic relations, whilst they support the conclusions drawn from our tests, are at variance with those derived by Flürscheim and Holmes from theirs.

(C) *Nature of the Side Reactions. Section (ii). Constructive Suggestions.*

(1) *Formation of* m-*Bromo-derivatives.*—An observation by Flürscheim and Holmes, which we are able to confirm, is that, when phenylbromocyanonitromethane is nitrated with acid so weak that side reactions strongly predominate, *m*-bromophenylbromocyanonitromethane is the principal product having an unde-

composed side chain. Flürscheim and Holmes's theory does not accommodate the direct formation of this major product, and they therefore postulate the following stages: (*a*) the original substance undergoes rearrangement, side-chain bromine passing to the nucleus; (*b*) another portion of the original substance loses side-chain bromine as hypobromous acid; (*c*) the hypobromous acid puts back bromine into the side chain of the rearrangement product. The inadequacy of this hypothesis will be clear from the foregoing criticism: thus (*a*) has been dealt with under (B, 2), (*b*) under (B, 3), and (*c*) under (B, 4). We suggest that *m-bromophenylbromocyanonitromethane is formed directly by nuclear attack of an external brominating agent, which either is, or depends on, free bromine.* Our reasons will now be summarised.

(i) *m*-Bromophenylbromocyanonitromethane is a major product (Flürscheim and Holmes; see also E, 9) under the conditions stated above.

(ii) In the nitration solution *a brominating agent is present* which is capable of introducing bromine into the *m*-position of a competing *m*-orienting benzene derivative (see B, 2; also E, 4).

(iii) When phenylbromocyanonitromethane decomposes *in the absence of any added reagent,* the volatile products contain large amounts of bromine and hydrogen bromide, and also a quantity of nitrosyl bromide sufficient for liquefaction and redistillation (see E, 10). The first is a brominating agent, the second would be in the presence of concentrated nitric acid, and the third is a potential brominating agent since it is a source of nascent bromine (Trautz and Dalal, *Z. anorg. Chem.*, 1920, **110**, 1). When these volatile products are drawn rapidly away by the use of a vacuum *there is practically no nuclear bromination* (see E, 11); wherefore the *m*-bromination is obviously far from being a simple intramolecular change; that is, it must be an extramolecular change.

(iv) We find, contrary to Flürscheim and Holmes, that the rate of formation of *m*-bromo-products varies largely with the concentration of the original substance (see B, 2; also E, 3). Thus the external brominating agent shown by (ii) to be *present,* is by (iii) and (iv) shown to be *responsible* for the *m*-bromination.

(v) Bromine is present in large quantities *in the nitration solution,* since its vapour is a major constituent of the evolved gases (see E, 6).

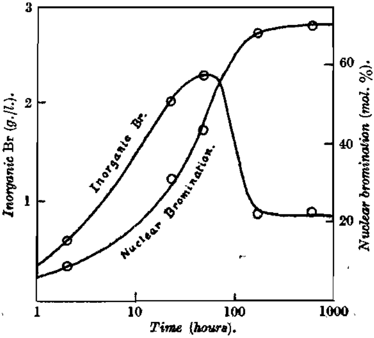
(vi) Nitrosyl bromide and hydrobromic acid, similarly proved to be present in the solution (see E, 6), must be sources of nascent bromine. That is, *bromine,* both actually and *in statu nascendi* is, by (v) and (vi), shown to be *present* in the nitration solutions.

(vii) The nuclear bromination occurring in nitric acid solution

is notably increased when the concentration of dissolved bromine is artificially augmented (see E, 7). Thus (Nitrations No. 31 and 32) the addition of one molecular proportion of bromine raised nuclear mono-bromination from 35·7 to 82·5%, and also gave rise to an appreciable amount of dibromination. Therefore, the bromine is evidently *capable* of effecting the nuclear bromination under the conditions obtaining.

(viii) The nuclear bromination occurring in nitric acid solution is notably decreased when the concentration of volatile substances is artificially decreased by aiding their escape (see E, 8). Thus the effect of aspiration with air, previously purified and saturated at the temperature of the experiment with the vapour of nitric

FIG. 2.



acid of the strength employed, was to reduce the *m*-bromination from 35·7 to 19·5% (Nitrations No. 32 and 33; compare 36). Aspiration with similarly treated oxygen-free nitrogen reduced the *m*-bromination from 43·1 to 23·3% (Nitrations No. 34 and 35). We conclude that the external brominating agent responsible for the *m*-bromination is a *volatile* substance.

(ix) During the reaction in nitric acid the concentration of inorganic bromine (that which is precipitable as silver bromide after removal of all organic material) first rises and then falls after the manner characteristic of an intermediate in consecutive reactions; meanwhile the concentration of nuclear bromination products rises to a maximum and then remains constant (see E, 5). This effect is shown in Fig. 2, which is drawn from the results

obtained in a group of experiments (Nitrations No. 22—26) in which the time-variation of the different bromination and nitration products was traced over a long period. Similar curves can be constructed from the results of Nitrations No. 27—30, which were similarly studied. We conclude that the external brominating agent responsible for the *m*-bromination is an *inorganic* substance.

Since the best known inorganic, volatile brominating agent is bromine, which has been proved both to be present and to be competent, we venture to connect it with the external brominating agent which has been shown to be responsible for the *m*-bromination.

(2) *Formation of* p-*Nitro-derivatives.*—The different orientation of the substituent in these derivatives shows that the mechanism of their formation must be radically different from that of the *m*-bromo-compounds. Flürscheim and Holmes, having postulated *intramolecular m*-migration of the bromine, fulfilled this obvious requirement by asserting that the *p*-nitro-compounds arise through the *extramolecular* substitution of a different aromatic compound. But this type of explanation will not serve; for we have shown that a brominating agent is present which, since it readily brominates even *m*-orienting compounds which undergo substitution comparatively slowly, would brominate to a still larger extent Flürscheim and Holmes's hypothetical intermediate, which undoubtedly would undergo *p*-substitution relatively very rapidly. Actually, very little *p*-bromination occurs. It would be beside the mark to argue that too little of the hypothetical intermediate is present; for then it would not explain what it was invented to explain, namely, the formation of a preponderance of *p*- over *m*-nitro-compounds, under conditions which also lead to a preponderance of *m*- over *p*-bromo-compounds. Thus the essential change leading to the formation of *p*-nitro-compounds is apparently *not* extra-molecular nitration by nitric acid, and once again we have to reverse Flürscheim and Holmes's conclusion and suggest that the *formation of* p-*nitro-compounds depends on an internal change involving group-migration*, in a sense to be considered later. Our reasons may be summarised as follows:

(i) The absence of any substantial quantity of *p*-bromo-products (see E, 4 and 9) appears to preclude the theory of ordinary substitution through a *p*-orienting intermediate.

(ii) Flürscheim and Holmes's hypothetical *p*-orienting intermediate is, in fact, instantly converted by bromine into a *m*-orienting compound (see E, 14).

(iii) Contrary to Flürscheim and Holmes, we find no product definitely attributable to ordinary nitration through a *p*-orienting intermediate. Excluding the small proportion of *op*-nitrophenyl-

bromocyanonitromethane conceivably arising from direct nitration of phenylbromocyanonitromethane (see B, 3), we cannot find in substantial quantity any derivative containing *two* nitro-groups, one in the *p*-position and the other in the side chain (see E, 9) (contrast bromination).

(iv) When nitric acid is *absent* during the progress of lateral decomposition, *op*-nitro-derivatives are still formed; and, moreover, they are formed in quantity (*e.g.*, 12%) sufficient to account, by means of a similar mechanism, for their production (*e.g.*, about 10%) by lateral decomposition in nitric acid solution (see E, 11).

By the phrase "internal change involving group-migration" we do not necessarily mean "intramolecular migration," although this would be included as a special case. A consideration of the mechanism of any real or so-called migration involves two major questions, namely, whether or no there is an internal change of structure, and, if there is, whether the group migrates within or without the molecule. *To illustrate: In the "rearrangement"* of *N*-chloroacetanilide there is neither an internal structural change * nor internal group-migration (Orton); in anionotropy the isomerisation of the kation is internal, but the group-migration is external (Burton, Ingold); in the rearrangement of imino-ethers both the structural change and the group-migration are internal (Chapman). An alternative expression of our suggestion is, therefore, that the formation of *p*-nitro-derivatives depends on a process belonging either to the second or to the third of the categories here exemplified (compare Ingold, Smith, and Vass, J., 1927, 1245). The matter is further discussed below.

(3) *Additional Details.*—The above attempt to elucidate the general character of the side reactions leaves several details undetermined, as, for instance, the form in which bromine is *originally* eliminated, later to become elementary bromine. It may be eliminated as nitrosyl bromide. This view would readily accommodate the formation of benzoyl cyanide as the main product of decomposition in the absence of nitric acid, and the presence in the gases of nitrosyl bromide, and the products of its dissociation, bromine and nitric oxide (E, 6 and 10):

$$C_6H_5\cdot CBr(NO_2)\cdot CN \longrightarrow C_6H_5\cdot CO\cdot CN + NOBr;$$

$$2NOBr \rightleftharpoons Br_2 + 2NO.†$$

Some of the eliminated bromine may also appear first as hydrogen

* Apart, of course, from the polarisations involved in any substitution by an external reagent.

† Nitrosyl tribromide, $NOBr_3$, would also be formed (reversibly), and its presence *may* be of importance in connexion with the intimate mechanism of bromination.

bromide, through the intervention of (subsequently regenerated) water, the organic product, α-nitro-α-cyanobenzyl alcohol, thus formed eliminating nitrous acid. Some hydrogen bromide and nitrogen peroxide are certainly evolved, in addition to bromine and nitric oxide (E, 6 and 10). This suggestion, which may be formulated thus,

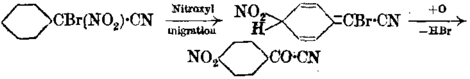
$$C_6H_5{\cdot}CBr(NO_2){\cdot}CN \longrightarrow C_6H_5{\cdot}C(OH)(NO_2){\cdot}CN \longrightarrow C_6H_5{\cdot}CO{\cdot}CN + HO{\cdot}NO,$$

was made to us by Dr. H. Burton. The first stage appears a *possible reaction for any benzyl halide*, and we have illustrated the postulated elimination of nitrous acid by converting α-bromo-α-nitro-α-phenylethane into acetophenone by the action of silver oxide and water (see E, 17):

$$C_6H_5{\cdot}CBr(NO_2){\cdot}CH_3 \longrightarrow C_6H_5{\cdot}C(OH)(NO_2){\cdot}CH_3 \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_3 + HO{\cdot}NO.$$

Here we have used a methyl group in place of the cyano-group in order to avoid hydrolysis of the carbonyl compound.

Various questions arose in connexion with the internal change *involving p-migration, such as whether the group-migration is* internal or external, and whether the displaced group is nitroxyl or nitrosyl. We have never observed a blue colour suggestive of the last hypothesis. In any event a concomitant oxidation must occur, either of the already displaced group, or of the residual side chain; for it has not been found possible to isolate an earlier product of these changes than *p*-nitrobenzoyl cyanide, the formation of which must involve the absorption of one atom of oxygen. We have illustrated (see E, 15) the possibility of the mechanism represented by



by demonstrating the formation of *p*-nitrobenzoyl cyanide (see also E, 16) by the action of reagents, known to be present in the above decomposition (namely, bromine and nitrogen peroxide), on a *p*-nitrophenyl derivative containing a reduced nitroxyl-free side chain (*p*-nitrophenylacetonitrile). The most probable view of the oxidation seems to be that the anion, *p*-$NO_2{\cdot}C_6H_4{\cdot}CBr{\cdot}CN$, intervening in the tautomerisation of the quinonoid product of nitroxyl-migration, achieves neutrality by ejecting a bromide ion, thus giving a bivalent carbon compound, *p*-$NO_2{\cdot}C_6H_4{\cdot}C{\cdot}CN$ (electron sextet), which would be autoxidisable to *p*-nitrobenzoyl cyanide.

A variant of the first of the suggested mechanisms for the formation of benzoyl cyanide from phenylbromocyanonitromethane consists in the elimination of nitroxyl bromide, and then the immediate oxidation by this substance of the bivalent carbon compound, C_6H_5·C·CN, so formed. The supposition that intermediates of this general type may arise by decomposition of the side chain in phenylbromocyanonitromethane renders intelligible the formation, not only of benzoyl cyanides, but also of stilbene derivatives—for the production of which we have obtained direct evidence by the isolation (see E, 12) of dicyanostilbene,

CPh(CN):CPh(CN).

The suggestions contained in this section are necessarily tentative.

(D) *Summary and Conclusions.*

(1) *Phenylbromocyanonitromethane.*—It has been shown (*a*) that Flürscheim and Holmes's alleged evidence that this substance passes by intramolecular migration of bromine into *m*-bromophenylcyanonitromethane is valueless, (*b*) that free bromine is present under all conditions in which *m*-bromo-products, including *m*-bromophenylbromocyanonitromethane, are formed, and (*c*) that a large body of cogent evidence exists (nine reasons, C, 1) which points unmistakably to the conclusion that these *m*-bromo-products are formed by extramolecular bromination of the nucleus.

(2) *Intramolecular* m-*Migration.*—It follows from (1) that no "proved case" of the intramolecular *m*-migration of a substituent from a side chain has as yet been discovered.

(3) *Theories of Aromatic Substitution.*—The intramolecular *m*-migration of a side-chain substituent, and indirect *m*-substitution dependent on this mechanism, are conceptions foreign to a theory of aromatic substitution which postulates inductive *m*-deactivation in *m*-orientation. The formation of *op*-products through an internal change involving the migration of a substituent from a normally *m*-directing side chain is, however, possible on this theory, since it envisages tautomeric *op*-activation (but not *m*-). The available evidence favours the suggestion that in the lateral decomposition of phenylbromocyanonitromethane *p*-nitro-products are formed in this way, the alleged contrary evidence of Flürscheim and Holmes having been controverted.

Experimental.

Preparation of Phenylbromocyanonitromethane (E, 1).

(1) *Method* (a).—In the earlier part of the investigation this substance was obtained by Flürscheim's method (*loc. cit.*), the samples being freshly prepared as required and analysed before

use (Found: C, 39·8, 40·1, 40·3; H, 2·1, 2·15, 2·05; Br, 32·6. Calc.: C, 39·8; H, 2·1; Br, 33·2%); but later it was found that a more uniform and stable product could be obtained by a method permitting the exclusion of water throughout the process.

Method (b).—Dry bromine (slightly less than the theoretical quantity) was added gradually to a stirred suspension of the finely *powdered dry sodium salt of phenylcyanonitromethane in dry* ether, and the filtered solution was evaporated at the ordinary temperature in a vacuum over phosphoric oxide. The product, a very pale yellow liquid, did not darken in colour and did not develop any sharp smell of benzoyl cyanide on being kept in air for more than one month; it is therefore much more stable than the product obtained by method (*a*). Also, the new process is more expeditious, since only a small volume of ether requires evaporation in the vacuum. As a precaution against the adventitious decomposition of any sample, however, the material was always freshly prepared as required.

Nitration of Phenylbromocyanonitromethane (E, 2—9).

(2) *Effect of Nitric Acid of Different Concentrations.*—(Series *a*. Nitrations No. 1—7.) These nitrations were all carried out under our formerly described conditions—except that the strength of the acid was varied—the products being isolated and analysed as recommended by Flürscheim and Holmes (oxidation method C was used throughout). The density of the nitric acid, free or almost free from nitrous acid, was determined with a 5 c.c. pyknometer to five significant figures, but the fifth figure is not accurate and is not quoted. The results are in the first table under (A), and the analytical data refer to acids obtained by oxidation of the nitration products from which the acid by-products have been removed by extraction with potassium hydrogen carbonate. The figures represent, not molecular percentages, but percentages by weight, since *the un-nitrated acids contained undetermined proportions of* *m*-bromobenzoic acid. Other numerical data are given in the table below.

(Series *b*. Nitrations No. 8—10.) These protracted nitrations were carried out with 16 parts of nitric acid at room temperature, and owing to the length of time the proportion of bromination is high. In these experiments the whole nitration product was oxidised. The results are given in the second table under (A), in which the figures for the bromo-acids include any nitro-*m*-bromobenzoic acids calculated as bromobenzoic acid, except in No. 8, in which the actual proportions of these acids were 21·1 and 17·0 mols. % respectively. The densities were determined as above.

Other details in connexion with nitrations No. 1—10 are in the following table :

Series.	Nitration No.	PBCN used (g.).	Acid product (g.).	Neutral product (g.).	C (%).	H (%).	m-NO_2-PBCN separated (%).	Material oxidised (g.).	Acids formed (g.).
(a)	1	4·490	—	4·045	41·1	2·2	None	3·185	1·751
	2	5·161	0·088	4·740	37·5	2·0	,,	3·610	2·092
	3	2·537	—	2·257	—	—	,,	1·940	1·081
	4	3·027	—	3·215	36·6	1·7	0·94	1·746*	0·992
	5	2·594	0·124	2·658	34·7	1·6	None	0·694	0·352
	6	3·403	—	3·670	—	—	49·0†	2·422	1·328†
	7	8·214	—	9·580	34·5	1·6	47·0	1·850*	0·791
(b)	8	4·00	3·360		—	—	None	3·260	2·588
	9	2·00	1·455		—	—	,,	1·455	1·299
	10	7·63	6·680		—	—	,,	1·580	1·359

* After separation of stated proportion of m-NO_2-PBCN.
† From different portions of neutral product.
A bar signifies " not determined."

(3) *Effect of Concentration of Phenylbromocyanonitromethane.*—(Series *a*. Nitrations No. 11—14.) The nitric acid used had $d_{4°}^{15°}$ 1·483. Four portions of the same specimen of phenylbromocyanonitromethane were simultaneously treated with the proportions of nitric acid indicated in the table under B, 2, and left in the same water-bath at room temperature for 20 hours. The solutions were worked up as under E, 2, the whole product being oxidised in each case. The yields and compositions are given below.

(Series *b*. Nitrations No. 15—17.) The nitric acid had $d_{4°}^{15°}$ 1·482. Three portions of the same specimen of phenylbromocyanonitromethane were simultaneously treated with the proportions of acid recorded under B, 2, and kept for 240 hours in the same bath at room temperature. The solutions were evaporated for a few hours over potassium hydroxide in a vacuum to remove the more volatile products and then extracted with ether. The whole products were oxidised as before, with the results recorded below :

					Composition of acids $R \cdot CO_2H$ (mols. %).				
Series.	Nitration No.	PBCN (g.).	Nitration products (g.).	Oxidation acids (g.).	R = C_6H_5.	op-$NO_2 \cdot C_6H_4$.	m-$NO_2 \cdot C_6H_4$.	m-$Br \cdot C_6H_4$.	NO_2-m-$Br \cdot C_6H_3$.
(a)	11*	4·137	—	2·220	97·7	1·1	0·0	1·2	0·0
	12	3·997	—	2·389	91·0	0·4	0·0	8·4	0·2
	13	4·009	—	2·324	78·0	0·7	1·4	19·0	0·9
	14	3·945	—	2·355	17·0	5·3	40·5	32·3	4·9
(b)	15	4·00	3·457	2·525	17·6	12·0	21·4	35·5	13·5
	16	4·00	3·360	2·588	0·0	20·1	41·8	21·1	17·0
	17	4·00	3·111	2·314	0·0	20·8	48·0	13·7	15·5

(*Note.*—A bar signifies " not weighed.")

(4) *Intramolecular Transference of Bromine.*—(Series *a*. Nitrations No. 18—20.) A specimen of nitric acid, $d^{18°}$ 1·45 (uncorr.), was used. Three nitrations were set up simultaneously, No. 18 with

1·90 g. of phenylbromocyanonitromethane and 16·0 g. of nitric acid, No. 19 with 3·00 g. of benzyltrimethylammonium picrate and 16·0 g. of nitric acid, and No. 20 with 1·90 g. of phenylbromocyanonitromethane, 3·00 g. of benzyltrimethylammonium picrate, and 16·0 g. of nitric acid; they were allowed to proceed in the same desiccator at the ordinary temperature for 800 hours. Potassium hydroxide was used in the desiccator, and the pressure in the stoppered nitration flasks was released from time to time.

(No. 18.) A solid had separated (0·1728 g.) which was identified as pure *m*-bromobenzoic acid (m. p. 150°). A further quantity of the same acid in a crude condition (m. p. about 140°) was obtained by the addition of about 250 c.c. of ice-water. The ethereal extract yielded a neutral fraction, which was not investigated, and an acid fraction (0·857 g.), which contained bromine and had m. p. 152—161°. By repeated crystallisation of the less soluble portion of this, a small amount of a still impure bromo-acid was obtained, the m. p. (about 220°) of which was raised by admixture with *p*-bromobenzoic acid.

(No. 19.) No crystallisation had occurred, and the solution, on being poured into water, gave 2·154 g. of a picrate, m. p. about 167°. A further 0·846 g. was obtained by treatment of the evaporated solution with sodium picrate. On crystallisation from alcohol, these picrate fractions yielded pure benzyltrimethylammonium picrate, m. p. 171°, showing that no considerable amount of nitration had occurred.

(No. 20.) The solid which had separated (0·161 g.) had m. p. 232° and was identified as *p*-nitrobenzoic acid. By addition of water to the solution, evaporation, and addition of sodium picrate, 2·20 g. of a picrate were obtained which after crystallisation from dilute alcohol yielded a product containing, according to an estimation of the bromine content, 95% of bromobenzyltrimethylammonium picrate. It had m. p. about 143° before purification and consisted essentially of the *m*-bromo-salt (below) (mixed m. p.).

(*Series b.*) *Preparation of m-bromobenzyltrimethylammonium salts.* *m*-Bromotoluene, prepared from *m*-toluidine, was brominated at 170—175° with slightly more than the theoretical amount of bromine, and the crude product was mixed with an excess of 33% alcoholic trimethylamine. The salt precipitated by the addition of ether was decolorised by charcoal in alcohol, reprecipitated with ether, and crystallised from absolute alcohol–ligroin; **m-*bromobenzyltrimethylammonium bromide*** was then obtained as white triangular prisms, m. p. 216° (Found: Ionisable Br, 26·2. $C_{10}H_{15}NBr_2$ requires ionisable Br, 25·9%). When this salt was

heated in a vacuum at 220—225°, decomposition took place. The product, presumably a mixture of *m*-bromobenzyl bromide and *m*-bromobenzyldimethylamine, on oxidation with hot 3% potassium permanganate solution yielded *m*-bromobenzoic acid, m. p. 147—148° (mixed m. p.). The quaternary *picrate*, obtained from the bromide by treatment with saturated aqueous sodium picrate, separated from absolute alcohol in small prisms, m. p. 150° (Found : C, 42·4; H, 3·9. $C_{16}H_{17}O_7N_4Br$ requires C, 42·0; H, 3·9%). *Benzyltrimethylammonium bromide*, prepared in the usual way, crystallised from alcohol–ligroin in thick rectangular plates, m. p. 235°, which depressed the m. p. of the *m*-bromo-bromide on admixture.

(No. 21.) Phenylbromocyanonitromethane (8·00 g.) and benzyltrimethylammonium picrate (12·60 g.) were nitrated together, with 35·4 c.c. of the nitric acid used for series (*a*), during 300 hours at room temperature. *p*-Nitrobenzoic acid, a neutral product (which had the odour of benzoyl cyanide and gave benzoic acid on oxidation), picric acid, and a series of picrate fractions (total, 11·46 g.) were isolated. A representative sample of the picrate fractions had a bromine content indicating the presence of 46% of *m*-bromobenzyltrimethylammonium picrate. The least soluble fractions, m. p. 148—149°, 149—150°, consisted essentially of this substance (mixed m. p.'s); they were compared with the synthetic specimen and converted into the corresponding bromides, which were similarly compared, and decomposed by heating in a vacuum at 220° to products which, when oxidised, yielded *m*-bromobenzoic acid, m. p. 146—149° (mixed m. p.). The most soluble picrate fraction, m. p. about 163°, contained only a trace of bromine and consisted essentially of unchanged benzyltrimethylammonium picrate (mixed m. p.).

(5) *Variation with Time of Organic Products and Inorganic Bromine*.—(Series *a*. Nitrations No. 22—26.) These were set up together by leaving a solution of 14·28 g. of phenylbromocyanonitromethane in 98 c.c. of nitric acid (*d* 1·46 uncorr.) at room temperature and withdrawing samples of 20 c.c. at intervals for analysis. Each sample was run on to ice prepared from distilled water, and the organic material extracted under standard conditions in halogen-free vessels with pure halogen-free ether. In the aqueous solution the bromine precipitable as silver bromide was estimated in the usual way. The organic product was separated into neutral and acid portions by extraction with potassium hydrogen carbonate solution. By weighing the two fractions separately it was shown that the acid portion was far too small to account for the proportion of *m*-brominated products, which are therefore proved to arise

by bromination of a neutral *m*-orienting substance. The neutral and the acid fractions were combined for analysis as under E, 2.

(*Series b. Nitrations No.* 27—30.) Phenylbromocyanonitromethane (24·26 g.) was nitrated with 166 c.c. of nitric acid (*d* 1·45 uncorr.) at the ordinary temperature. Samples of 20 c.c. were withdrawn at intervals as before, but in this series the order of addition of ether and silver nitrate was inverted, and the organic product was not separated into neutral and acid portions, but was weighed all together and oxidised as above. A qualitative test after 2·5 hours showed the presence of free bromide ions.

The results obtained in both series are recorded in the following table :

Series.	Nitr. No.	Time (hrs.).	*Inorg.* Br (g./l.).	*Organic (g./c.c.).* Neutral.	Acid.	Acids by oxidn. (g./c.c.).	Composition of acids $R \cdot CO_2H$ (mols. %). R = C_6H_5.	*op*-$NO_2 \cdot C_6H_4$.	*m*-$NO_2 \cdot C_6H_4$.	*m*-$Br \cdot C_6H_4$.	NO_2-*m*-$Br \cdot C_6H_3$.	Nuclear by-products.
(*a*)	22	2	0·61	0·1215		0·0593	82·0	8·5(?)	0·3	9·1		9·1
	23	23	2·03	0·1105	0·0046	0·0578	63·5	3·1	1·6	31·8		31·8
	24	48	2·32	0·1112	0·0060	0·0877	51·6	4·0	1·0	41·0	2·4	43·4
	25	168	0·86	0·0946	0·0145	0·0919	24·5	5·0	2·3	63·8	4·4	68·2
	26	360	0·92	0·0600	0·0407	0·0897	22·3	3·8	3·9	60·3	9·7	70·0
(*b*)	27	23	1·19	0·1036		0·0054	61·0	5·4	1·8	29·2	2·3	31·5
	28	49	2·03	0·1000		0·0639	55·0	2·8	1·0	37·3	3·9	41·2
	29	144	2·29	0·1093		0·0773	26·6	1·2(?)	2·0	56·1	14·0	70·1
	30	312	1·19	0·1017		0·0759	24·8	3·1	5·0	49·8	17·3	67·1

The spent liquors of each of these nitrations were treated with silver nitrate under the conditions of Flürscheim and Holmes's recorded tests for hypobromous acid. For the first few seconds the silver bromide precipitate remained colloidal, and appeared as a haze by transmitted light ; soon, however, it began to flocculate, and, as is usual with silver bromide precipitates, the process was greatly hastened by shaking. An artificial solution of redistilled bromine in halogen-free aqueous nitric acid, when treated with a little halogen-free ether and silver nitrate under the same conditions, behaved, contrary to Flürscheim and Holmes's statement, in exactly the same way.

(6) *The Volatile Products.*—Flürscheim and Holmes do not record the formation, in large quantity, of a number of volatile products of the action of nitric acid on phenylbromocyanonitromethane. Many of our nitrations, including the series 22—30, were carried out in an all-glass apparatus in which the volatile products could be drawn off and examined. The gases identified were bromine (formation of styrene dibromide, m. p. and mixed m. p. 68°, from styrene in carbon tetrachloride), hydrogen bromide (usual test, with halogen-free reagents, after removal of bromine) nitrogen peroxide (colour in absence of free bromine and oxygen

formation of nitrite and nitrate with alkali; formation of deep blue nitrosite with tetramethylethylene in carbon tetrachloride), and nitric oxide (colour on addition of oxygen after removal of bromine and nitrogen peroxide). The presence of bromine and nitric oxide proves the presence of nitrosyl bromide.

(7) *Effect of Addition of Bromine.*—(Nitrations No. 31, 32.) These experiments were set up simultaneously, the same samples of phenylbromocyanonitromethane and nitric acid (10 parts; $d_{4^\circ}^{15^\circ}$ 1·483) being used, and allowed to proceed in sealed tubes for 36 hours at the ordinary temperature. The whole products were oxidised in each case. In No. 31, bromine (1 mol.) was added, and the un-nitrated acids, recovered after oxidation with permanganate and reduction with titanous chloride, had a bromine content equivalent to more than 100% of monobromobenzoic acid; the composition of the mixture was therefore calculated as that of a mixture of mono- and di-bromobenzoic acids. In No. 32, no additional bromine was introduced, and the un-nitrated acids, which had a much lower bromine content, were taken as a mixture of benzoic and bromobenzoic acids. The following are the compositions of the acids $R\cdot CO_2H$, calculated as mols. % on these assumptions:

Nitration.	PBCN (g.).	Acids (g.).	R = C_6H_5.	*op*- $NO_2\cdot C_6H_4$.	*m*- $NO_2\cdot C_6H_4$.	C_6H_4Br.	$NO_2\cdot C_6H_3Br$.	Total mono-bromo-.	$C_6H_3Br_2$.
31	4·160	3·429	0·0	0·3	2·5	71·1	11·4	82·5	14·7
32	4·050	1·811	22·7	2·0	39·6	31·8	3·9	35·7	0·0

(8) *Effect of Aspiration with Air and Nitrogen.*—(Nitrations No. 32—36.) Simultaneously with No. 32, another nitration, No. 33, was set up with the same materials in the same proportion, but in an all-glass apparatus permitting the passage of a gas through the solution. The nitration was carried out at the same temperature and during the same period as No. 32, but throughout the whole time air, previously passed over decarbonating and drying agents and then through a sample of the same nitric acid, $d_{4^\circ}^{15^\circ}$ 1·483, as that used for the nitration, was drawn through hy a water-pump, a capillary tube being used as a precaution against back-diffusion and irregular flow.

Two more nitrations, No. 34 and 35, were set up simultaneously with each other, the same sample of phenylbromocyanonitromethane and the same nitric acid ($d_{4^\circ}^{15^\circ}$ 1·483; 10 parts) being used —No. 34 in a loosely stoppered bottle, and No. 35 in the aspiration apparatus—and allowed to proceed at the same temperature (room) during the same time (36 hours). Nitrogen, taken from a cylinder, freed from oxygen by passage through alkaline pyrogallol, dried, and saturated with the vapour of the nitric acid used for nitration, was passed through the nitration solution throughout the period,

capillaries being used to buffer the stream, and slight suction from a water-pump serving to maintain the conditions of pressure the same as in No. 33.

Experiment No. 36 was a duplicate of No. 33, except that the temperature, and the rate of bubbling of the air, were only approximately repeated. Since the main object was to obtain an additional check on the reduced proportion of *m*-bromination, indicated by experiments 33 and 35, the analysis was shortened by estimating *the small amount of nitro-m-bromo-acids as m-bromobenzoic acid along with the main portion of this substance.* The error thus introduced makes the mols. % of *m*-bromo-products slightly high, so that the corresponding estimate of the reduction of *m*-bromination caused by aspiration is on the conservative side.

All analyses of this series were carried out on the *whole* nitration products, as under E, 2. The results are shown in the table, in which the brackets indicate pairs of experiments in which all conditions, other than those relating to the escape of volatile products, were identical:

Nitration.	Aeration and aspiration.	PBCN (g.).	Oxidation acids (g.).	Composition of acids $R\cdot CO_2H$ (mols. %). R = C_6H_5.	*op*-$NO_2\cdot C_6H_4$.	*m*-$NO_2\cdot C_6H_4$.	*m*-C_6H_4Br.	NO_2-*m*-C_6H_3Br.
{32	Sealed tube	4·050	1·811	22·7	2·0	39·6	31·8	3·9
{33	Air passed	5·040	2·097	51·2	4·6	24·7	14·6	4·9
{34	Loosely stoppered	3·979	2·296	17·1	3·6	36·2	39·2	3·9
{35	Nitrogen passed	4·014	1·762	22·9	3·8	50·0	21·8	1·5
36	Air passed	4·145	2·343	47·8	3·1	31·8	17·3 (both columns)	

(9) *Nuclear Substitution Products with an Unaltered Side Chain.*—(Nitration No. 37.) In this experiment we followed the procedure recommended by Flürscheim and Holmes for the separation and analysis of the products with an unaltered side chain, but, contrary to their statement, encountered no difficulty in estimating these substances by direct oxidation to the corresponding substituted benzoic acids; the results obtained by Flürscheim and Holmes's method were therefore checked by this more direct method.

Phenylbromocyanonitromethane (8·86 g.) was nitrated with 120 c.c. of nitric acid, $d_{4}^{15°}$ 1·480, for 120 hours at room temperature. Benzoic acids were removed from the ethereal extract of the product by shaking with 5% potassium hydrogen carbonate solution, and a portion (3·81 g.) of the neutral residue (7·35 g.) was shaken with ether and a solution of potassium iodide (12 g.) in water (60 c.c.). The aqueous solution was shaken for 1·5 hours with 10% aqueous potassium hydroxide, and then oxidised with boiling 3% potassium permanganate solution, that part of the iodine thus produced which did not escape from the solution being destroyed

by sulphur dioxide after the oxidation. The ethereal solution, when freed from iodine by washing with aqueous sodinm thiosulphate, dried, and evaporated, left a residue weighing 1·534 g. The complete neutral product thus contains 59·8% of arylbromocyanonitromethanes and 40·2% of benzoyl cyanides, etc. In the following table the figures for *op*-nitro-derivatives may be slightly high (*e.g.*, 2%) and those for bromonitro-products correspondingly low, owing to incomplete hydrolysis under our conditions of the salts of the bromoaminobenzoic acids in acid solution. The row marked "calc." contains percentages indirectly calculated in accordance with Flürscheim and Holmes's procedure. The compositions of the acids $R{\cdot}CO_2H$, obtained from the various fractions of the nitration product, are in mols. %.

Product of nitration No. 37.	R = C_6H_5.	*op*- $NO_2{\cdot}C_6H_4$.	*m*- $NO_2{\cdot}C_6H_4$.	*m*- C_6H_4Br.	$NO_2{\cdot}C_6H_3Br$.
(*a*) Whole neutral (taken as 100% by weight)	1·5	7·1	43·0	39·7	8·7
(*b*) Bromocyanonitromethanes (59·8% by weight)	4·3	7·0	54·8	25·1	8·8
(*c*) Benzoyl cyanides, etc. (40·2% by weight)	0·3	4·3	16·7	71·0	7·7
(*d*) Bromocyanonitromethanes (calc.)	2·4	9·0	60·7	18·6	9·3

The non-nitrated benzoic acids recovered in the course of the analyses (*b*) and (*c*) were qualitatively examined. Each consisted of nearly pure *m*-bromobenzoic acid, which was obtained pure (m. p. and mixed m. p.) by one crystallisation from chloroform in both cases. This confirms the analogous result recorded under E, 4, and shows that, contrary to Flürscheim and Holmes's conclusion, *op*-orienting compounds are not present during these nitrations.

Lateral Decomposition of Phenylbromocyanonitromethane in the Absence of Nitric Acid (E, 10—12).

(10) *Decomposition at Atmospheric Pressure.*—(*a.* At the ordinary temperature.) Phenylbromocyanonitromethane (8·86 g., prepared by method *a* : see E, 1) was allowed to decompose at the ordinary temperature in an apparatus similar to that used for the examination of the gaseous products formed on nitration (see E, 6). Bromine, hydrogen bromide, nitric oxide, and nitrogen peroxide were identified, and the partly solid residue remaining after 3 months (6·78 g.) yielded benzoyl cyanide, *p*-nitrobenzoyl cyanide and *p*-nitrobenzoic acid as the main isolable products (m. p. and mixed m. p. in each case).

(*b.* At 75—80°.) Flürscheim and Holmes identified bromine and nitric oxide amongst the volatile products; we find that

hydrogen bromide, nitrogen peroxide, and nitrosyl bromide are also produced. The decomposition of phenylbromocyanonitromethane (17·0 g.) was allowed to proceed in an all-glass apparatus in which the volatile products condensable at − 35° were collected in a bulb (subsequently to be used as a distilling flask) cooled in liquid ammonia, whilst the products which were not thus condensable passed into an eudiometer. In the non-liquefied gaseous portion, hydrogen bromide and nitric oxide were identified as described previously. The deep brown liquefied product was distilled by applying a cooling bath to a series of sealed-on bulbs to be used as receivers, and placing around the distilling bulb a water-bath, which, initially at 0°, was slowly heated. The bulbs were caused successively to function as receiver by a simple mechanism involving the rotation of a well-ground glass joint, and the fractionation was controlled by a thermometer, the very small bulb of which, touching the bottom of the distilling bulb, was totally immersed in the boiling liquid until near the end of the distillation. Finally, the bulbs were cut off, and their contents tested. The first fraction (small) had b. p. − 2° (constant), and on decomposition with distilled water gave a solntion which, after being

tio.
32 ...e alkaline with halogen-free potassium hydroxide, was proved
33 ...ntain bromide and nitrite but no nitrate (recorded b. p. of
34 ... bromide, − 2°). The second fraction (large) had b. p.
35 Ni...and its solution in alkali yielded positive tests for nitrite
36 Air p... (recorded b. p. of nitrogen peroxide, 22°). The third ...ll) had b. p. up to 54°, mostly above 50°, and con-

(9) *Nuclear S*... containing a little nitrogen peroxide (proved as —(Nitration No. 3...urth fractions). The fourth fraction (large), cedure recommended proved to be bromine by its odour, volatility, and analysis of the pr...from an iodide, and the formation of styrene contrary to their stateme...ed m. p.) from styrene.
these substances by direct o...the decomposition flask was placed in a benzoic acids; the results ...her quantity of volatile material, and method were therefore check... pressure; benzoyl cyanide (4·7 g.)

Phenylbromocyanonitromet..., together with an impure fractio... 120 c.c. of nitric acid, $d_{4}^{15°}$ 1·48...nzoyl cyanide crystallised (m. p. 116 Benzoic acids were removed from...), and a residue which decomposed duct by shaking with 5% pot... *Vacuum*.—The decomposition wa... and a portion (3·81 g.) of the..., and the residue oxidised by Flür with ether and a solution of C. The acids contained benzoic aci... (60 c.c.). The aqueous solu...ic acid (11·9 mols. %), and *m*-bromo 10% aqueous potassium hydr...at no *m*-nitro- or nitro-*m*-bromo-acid 3% potassium permanganate this experiment of any possible volatil produced which did not esca...tion of *op*-nitro-products is similar t

(somewhat higher than) that found by Flürscheim and Holmes for decomposition at the ordinary pressure.

(12) *Decomposition in the Presence of Phosphoric Oxide.*—This experiment, although it represents an unsuccessfnl (and very crude) attempt to arrest the decomposition by drying, is of interest inasmuch as it led to the isolation of dicyanostilbene. A concentrated ethereal solution of phenylbromocyanonitromethane (prepared by method *b*; see E, 1) was dried with phosphoric oxide for 2 days, and then transferred to a dried bulb containing fresh pentoxide. The ether was removed by distillation and the residue decomposed at about 75°. After removal of most of the benzoyl cyanide from the product by distillation up to 100°/9 mm., the residue was extracted with ligroin. The crystalline substance thus obtained, after recrystallisation from the same solvent, had m. p. 155—156°, both alone and after admixture with an authentic specimen of dicyanostilbene.

Observations on Phenylcyanonitromethane (E, 13, 14).

(13) *Decomposition in the Absence of Reagents.*—(*a.* Isolation of benzoyl cyanide.) An ethereal extract of the nitro-compound, prepared from 4·0 g. of its purified sodium salt, was evaporated, and the residue warmed to assist decomposition and finally heated on the steam-bath for a short time. The residue on distillation yielded a small fraction, b. p. about 110°/24 mm., which solidified and was identified as benzoyl cyanide, m. p. 32—34°. Extensive decomposition occurred on continuing the distillation.

(*b.* Evidence of nitroxyl-migration.) The above experiment was repeated, but the residue, instead of being distilled, was shaken for 3 hours with 10% potassium hydroxide solution, and the product oxidised with permanganate. The acids thus obtained contained 10% by weight of an acidic gum which was insoluble both in ether and in hot hydrochloric acid. The remaining 90% of the acids had the following composition: benzoic acid 75·3 mols. %, *m*-nitrobenzoic acid 0·3 mol. % (?), and *op*-nitrobenzoic acids 24·4 mols. %.

(14) *Action of Bromine.*—An ethereal solution of the nitro-compound reacted instantly with one molecular proportion of bromine in freshly prepared ethereal solution. The product obtained from the ethereal solution, after washing with water and drying, had the properties of phenylbromocyanonitromethane.

Formation of Benzoyl Cyanide and its Analogues (E, 15—17).

(15) *Conversion of* p-*Nitrophenylacetonitrile into* p-*Nitrobenzoyl Cyanide.*—*p*-Nitrophenylacetonitrile (5 g.) was heated to 120° (bath temperature) until fused, and then at 100—110° during the

gradual addition of dry bromine (6 g.) by a delivery tube dipping under the surface. Heating at the same temperature was continued until the evolution of hydrogen bromide ceased, and the cooled product was shaken with about 200 c.c. of dry ether, which dissolved all but a small amount of viscous oil. The residue from the ether rapidly crystallised, and after a further crystallisation from ether–ligroin yielded p-*nitrophenylbromoacetonitrile* as small cubes, m. p. 96° (Found : C, 40·5 ; H, 2·2. $C_8H_5O_2N_2Br$ requires C, 39·8 ; H, 2·1%).

An attempt to effect the bromination at 140—150° by means of bromine vapour carried in a current of carbon dioxide led to the formation of di-*p*-nitrodicyanostilbene, which crystallised from acetone and then melted at 275°.

The ether-insoluble oil, the residue obtained on evaporation of the ethereal extract, and the pure bromo-compound were separately treated for 1 hour at 80—90° with the oxides of nitrogen evolved from arsenious acid and nitric acid (*d* 1·35, uncorr.). The products were distilled under diminished pressure, and, in the first two cases, distillates were obtained which solidified and after crystallisation from ligroin yielded pure *p*-nitrobenzoyl cyanide (m. p. and mixed m. p. 116—117°). The same substance was obtained when *p*-nitrophenylacetonitrile was treated at 100—110° for 1 hour with a mixture of bromine vapour and the oxides of nitrogen generated as above. In the later stages of the above distillations at 5 mm. extensive decomposition occurred, making it impossible to identify the remainder of the material.

(16) *Conversion of Mandelonitrile into Benzoyl Cyanide.*—When mandelonitrile was warmed on the steam-bath with a small proportion of bromine, hydrogen bromide was evolved and a very small quantity of a solid substance crystallised in the condenser. The liquid product was mixed with water and extracted with ether, and the acidic substances were removed from the ethereal extract by washing with potassium hydrogen carbonate solution. When the residue from the ethereal solution was distilled, the small fraction, b. p. 100—120°/24 mm., which was collected before the onset of decomposition, crystallised on cooling and yielded benzoyl cyanide, m. p. and mixed m. p. 32—34°.

(17) *Conversion of α-Bromo-α-nitro-α-phenylethane into Acetophenone.*—The bromonitro-compound (Baker and Ingold, *loc. cit.*) was first treated in the cold, and then gently warmed, with excess of moist silver oxide. The product was extracted with ether, freed from acids by washing with potassium hydrogen carbonate solution and, after evaporation of the ether, distilled under diminished pressure. The initial portion of the distillate, b. p. about 120°/1[illegible]

mm., on treatment with aqueous semicarbazide acetate, yielded a opious precipitate of acetophenonesemicarbazone (m. p. and mixed m. p.).

We wish to thank the Chemical Society for a grant in aid of this work.

THE UNIVERSITY, LEEDS. [*Received, January 14th*, 1929.]

LXIII.—*The Mobility of Symmetrical Triad (Prototropic) Systems. Part IV. Mobility in the Simple Three-carbon System terminated by Aryl Groups.*

By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE.

THE importance, from the point of view of the modern theory of eactivity-distribution in molecules, of the study of equilibria in imple * three-carbon prototropic systems has recently been mphasised (Ingold and Rothstein, this vol., p. 8), but no systematic xamination of the subject has yet been taken up. The main vailable examples of three-carbon prototropy may be grouped as ollows: (I) Indene, its derivatives and analogues (Ingold and Piggott, J., 1923, **123**, 1469; Goss and Ingold, J., 1928, 1268); II) propenylbenzene and its substitution products (Tiffeneau, *Compt. rend.*, 1904, **139**, 482; Shoppee, J., 1928, 2567; *inter alia*); III) propenylammonium derivatives (Ingold and Rothstein, *loc. cit.*).

(I.)

$Aryl{\cdot}CH_2{\cdot}CH{:}CH_2$ (II)

$R_3\overset{+}{N}{\cdot}CH_2{\cdot}CH{:}CH_2$ (III.)

(IV.) $Aryl{\cdot}CH_2{\cdot}CH{:}CH{\cdot}Aryl'$

$R_3\overset{+}{N}{\cdot}CH_2{\cdot}CH{:}CH{\cdot}\overset{+}{N}R_3'$ (V.)

The great mobility of systems (I) renders them unsuitable for nvestigations on the position of equilibrium. Systems (II) and III), on the other hand, undergo isomeric change only in the resence of an added proton-attractor (usually ethoxide ions †), nd the equilibrium, once attained, can readily be fixed by destruction of the catalyst. The difficulty with regard to these systems, however, is that the equilibrium is too one-sided to permit of ccurate determination. It therefore seemed that by the introduc-

* The adjective is introduced to indicate the exclusion of pentad "three-carbon systems" (*e.g.*, pentad keto-enol, CH·C:C·C:O, etc.).

† The order of proton-affinity of the more commonly employed alkaline atalysts is OH′ < OMe′ < OEt′, and illustrations of these inequalities are given n this paper.

tion of a balancing group, as in (IV) or (V), series might be obtained in which both the mobility and the position of equilibrium would be of a convenient order. This paper records a preliminary investigation in which systems of type (IV) have been quantitatively studied with tolerably satisfactory results.

The methoxyhydrocarbons (VI) and (VII) were originally described by Ingold and Piggott (*J.*, 1922, **121**, 2381): they underwent no interconversion at 220—230°, and each yielded its own dibromide. We have confirmed these results and found, further, that no interconversion occurs in the presence of hot dilute alkali solution, and that on ozonolysis each isomeride yields exclusively products corresponding to its constitution. These observations establish the stability of the isomerides under the condition which we have employed to isolate and examine the products of their partial or complete equilibration. Moreover, we found that each methoxyhydrocarbon could be quantitatively regenerated, without any interconversion, from its pure dibromide by the action of zinc dust, and this gave the means of obtaining the isomerides in the high degree of purity required for the study of their isomerisation by a physical method.

$$p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot CH{:}CHPh \rightleftharpoons p\text{-MeO}\cdot C_6H_4\cdot CH{:}CH\cdot CH_2Ph$$

(VI, 29·5%.) (VII, 70·5%.)

Interconversion was effected in 1·45*N*-ethyl-alcoholic sodium ethoxide at 85°, and, after 4 hours or longer at this temperature, mixtures were obtained which gave, on ozonolysis, products derived from both isomerides, and yielded mixtures of dibromides from which, even when (VI) was the starting point, up to 58% of the dibromide of (VII) could be isolated in a state of purity. The attainment of equilibrinm was thereafter studied refractometrically. The coefficient (k_1+k_2) for the velocity of interconversion was 0·79 hour^{-1}, and the equilibrium ratio (k_1/k_2) was 0·42, the corresponding percentages being as indicated beneath the formulæ above.

During the preparation of the methoxyhydrocarbons considerable quantities of the β-carboxy-derivatives (VIII and IX) were accumulated, and it appeared of interest to examine the equilibration of these under the conditions used for the methoxyhydrocarbon, since the position of the carboxyl group is such that neither substance is a pentad keto-enol tautomeride. This was done (by thermal analysis), but the composition–time curves exhibited a curious semirectilinear character, which was traced to the separation of the sodium salts of the acids under the conditions used: the equilibration was non-homogeneous. Therefore, although the same equilibrium mixture (indicated below the formulæ) was obtained

from each isomeride, the numerical data given in the experimental portion cannot be expressed as velocity coefficients:

$$\underset{\text{(VIII, 44·0\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot \overset{CO_2H}{C}:CHPh} \underset{\text{anions}}{\overset{\text{as}}{\rightleftharpoons}} \underset{\text{(IX, 56·0\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH:\overset{CO_2H}{C}\cdot CH_2Ph}$$

The acids were therefore converted into their methyl and ethyl esters, and the purity of these was proved by finding conditions in which they could be hydrolysed quantitatively to the corresponding pure acids. The same method of hydrolysis, combined with thermal analysis of the acids, gave a convenient method for the analysis of mixtures of isomeric esters. Observations on the interconversion of the isomeric methyl esters in the presence of methyl-alcoholic sodium methoxide at the b. p. and at 100° showed that this catalyst, although it effected some isomerisation at the higher temperature, was inconveniently slow in its action. The ethyl esters were therefore selected for quantitative study. They readily came into equilibrium at 85° in the presence of alcoholic sodium ethoxide of the concentration used for the methoxyhydrocarbons, and the composition–time curves exhibited the normal unimolecular character. The velocity coefficient (k_1+k_2) was 0·0585 hour^{-1}, and the equilibrium ratio (k_1/k_2) was 0·770, the corresponding percentages being as shown beneath the following formulæ:

$$\underset{\text{(X, 43·5\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot \overset{CO_2Et}{C}:CHPh} \rightleftharpoons \underset{\text{(XI, 56·5\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH:\overset{CO_2Et}{C}\cdot CH_2Ph}$$

The theoretical significance of these results, in so far as it is not apparent from previous publications, will be discussed on a future occasion.

EXPERIMENTAL.

(1) *Interconversion of the Methoxyhydrocarbons.*

α-p-*Methoxyphenyl-γ-phenyl-Δ^β-propene* (VI).—*p*-Methoxycinnamic acid was prepared in good yield by condensing *p*-anisaldehyde with malonic acid in pyridine solution on the steam-bath with the addition of a little piperidine, and reduced (220 g.) at about 45° with 3% sodium amalgam (15 kg.) to the dihydro-acid, which was crystallised from 30% acetic acid below 60° (yield, 200 g.), and converted into its sodium salt. Ingold and Piggott's method of condensing this salt with benzaldehyde was modified to the following. The melt obtained by heating the salt (165 g.), benzaldehyde (105 g.), and acetic anhydride (105 g.) successively for 5 hours at 150°, 4 hours at 160°, and 1 hour at 170° was poured into a solution of excess of crystallised sodium carbonate and extracted with ether. The extract was washed with 2*N*-sodium hydroxide

and water, dried, and evaporated, and the residue carefully distilled in a vacuum by means of a metal-bath and a short column. The methoxyhydrocarbon was obtained (10·5 g.) as a pale yellow liquid, b. p. 211—213°/15 mm., $n^{26°}_{5461}$ 1·60194; an independent preparation had b. p. 208—211°/14 mm. and $n^{26°}_{5461}$ 1·60194. It was converted into its dibromide, the m. p. of which was raised to the constant value of 94° by repeated crystallisation from ligroin (Found: C, 50·0; H, 4·2. Calc.: C, 50·0; H, 4·2%). The purified bromide was treated with excess of zinc dust, followed by a small amount of "molecular" silver in boiling absolute alcohol, and the methoxy-compound extracted with ether from the diluted and acidified filtrate. It had b. p. 179—180°/3 mm. and $n^{26°}_{5461}$ 1·60246. The regenerated methoxyhydrocarbon yielded the same crystalline dibromide, and repeated distillation, and boiling for several hours with dilute sodium hydroxide solution, did not alter this property or the refractive index. Successive treatment with ozone and water yielded benzaldehyde (semicarbazone instantly precipitated), *p*-methoxyphenylacetaldehyde, and benzoic acid, but no *p*-methoxyphenylacetic acid.

α-Phenyl-γ-p-methoxyphenyl-Δ^{β}-propene (VII).—Sodium β-phenylpropionate (225 g.), *p*-anisaldehyde (160 g.), and acetic anhydride (160 g.), condensed as in the last example, yielded 46 g. of the methoxyhydrocarbon, b. p. 211—215°/14—15 mm., $n^{26°}_{5461}$ 1·60659. This may be a mixture of geometrical isomerides, since the purified dibromide, m. p. 119°, on treatment with zinc and silver as described above, gave specimens having b. p. 185—186°/3 mm. and $n^{26°}_{5461}$ 1·60598. Its stability to heat and aqueous alkali was proved as for the isomeride. Ozonolysis yielded anisaldehyde (semicarbazone instantly precipitated), phenylacetaldehyde, and anisic acid, but no phenylacetic acid.

Interconversion.—Either methoxyhydrocarbon (1 part) was heated at 85° for various times up to 18 hours with a solution of sodium (1 part) in ethyl alcohol (30 parts). The product was poured into water and extracted with ether and the extract was washed with calcium chloride solution, dried, and evaporated. The residual oil was then completely distilled under a pressure of about 1 mm.

Qualitative Examination.—Some of the products thus obtained were converted into their dibromides, from which considerable quantities (up to 58%) of the dibromide of α-phenyl-γ-*p*-methoxyphenylpropene were isolated when the period of heating of either methoxyhydrocarbon had been 4 hours or longer. Other products were also submitted to ozonolysis; benzoic and anisic acids were then obtained and partly separated, and likewise the rapidly precipitated semicarbazones of benzaldehyde and anisaldehyde.

Quantitative Examination.—The linearity of the mixture law for the refractive indices of the isomeric methoxyhydrocarbons (VI and VII) was confirmed experimentally, and the interconversion was then followed refractometrically. The drum of the Pulfrich instrument was used as in the measurement of dispersion, so that differences of refractive index could be observed with greater accuracy than their absolute values; by using a narrow auxiliary slit, and carefully focusing the green line from a powerful mercury arc on the cross-wires, very accurate settings could be obtained. All the measurements were taken over a short interval of time; the temperature recorded, which is that of the water-jacket of the refractometer, was constant throughout the measurements.

Refractive Indices of the Methoxyhydrocarbons and their Mixtures.

VI (%)	0·0	25·5	73·0	100·0
$n_{5461}^{26\cdot0^\circ}$	1·60598	1·60511	1·60342	1·60246
VI (% calc.) *	—	25·0	73·0	—

* From linear law.

Interconversion of Isomerides.

Isomeride used.	Time at 85° with NaOEt (hrs.).	$n_{5461}^{26\cdot0^\circ}$.	Isomeride VI (%).	$k_1 + k_2$ (hour^{-1}).
VII	0·0	1·60598	0·0	—
	1·0	540	16·5	0·82
	2·0	519	23·0	0·76
	4·0	498	28·5	0·84
	18·0	494	29·5	—
VI	18·0	494	29·5	—
	0·0	246	100·0	—

Equilibrium : VI (29·5%) $\rightleftharpoons$ (70·5%) VII; velocity coefficient $(k_1 + k_2) =$ 0·79 hour^{-1}; $k_1/k_2 = 0{\cdot}42$; $k_1 = 0{\cdot}23$; $k_2 = 0{\cdot}56$.

(2) *Interconversion of the Methoxy-acids.*

α-p-*Methoxybenzylcinnamic Acid* (VIII).—An almost pure specimen (23·5 g.) of this acid was obtained by acidifying the sodium hydroxide washings obtained in the preparation of α-*p*-methoxyphenyl-γ-phenylpropene, and a further quantity was isolated from the sodium carbonate solution as described by Ingold and Piggott (m. p. 165·5°).

p-*Methoxy*-α-*benzylcinnamic Acid* (IX).—This acid was isolated and purified exactly as described by Ingold and Piggott, attempts to employ fractional crystallisation or extraction being unsuccessful (m. p. 171·5°).

Interconversion.—Interconversion was effected by heating either acid with sodium ethoxide, under the conditions described for the methoxyhydrocarbons, for various times up to 48 hours. Ice-water and hydrochloric acid were added, and the organic acids extracted

completely with pure ether. The extract was dried and evaporated, and the last trace of ether removed at 100°.

Qualitative Examination.—Products obtained by heating α-*p*-methoxybenzylcinnamic acid with sodium ethoxide for 24 hours or longer under the above conditions had m. p. about 130—140° (Found: C, 75·5; H, 5·9. Calc.: C, 76·1; H, 6·1%). Three crystallisations from dilute alcohol gave crystals, m. p. 171°, consisting of pure *p*-methoxy-α-benzylcinnamic acid. Other portions of these and similar products obtained from the same initial acid were treated with ozonised oxygen in glacial acetic acid solution for 24 hours, and the ozonide was decomposed with water. The products were separated into neutral and acid portions with ether and sodium carbonate. The main constituent of the acid fraction was *p*-anisic acid, which was readily purified by crystallisation from alcohol. The neutral portion yielded an immediate precipitate of semicarbazones, the major constituent of which was anisaldehyde-semicarbazone, m. p. 203°; the soluble semicarbazones were not examined. These experiments afford qualitative proof of the reaction in the direction (VIII) ⟶ (IX).

Products obtained by heating *p*-methoxy-α-benzylcinnamic acid with sodium ethoxide for 24 hours or longer as indicated above were oxidised at 0° with the theoretical quantity of dilute permanganate solution, and the oxidation acids isolated in the usual way. Extraction with warm ligroin yielded phenylacetic acid, which separated from the solvent on cooling, and from the sparingly soluble residue benzoic acid was sublimed and identified. The residue, principally *p*-anisic acid, was purified by crystallisation from dilute alcohol. The isolation of benzoic acid indicates the presence of α-*p*-methoxybenzylcinnamic acid in the material oxidised. A control oxidation experiment with pure *p*-methoxy-α-benzylcinnamic acid gave the same results except that no benzoic acid could be removed by sublimation. This proves that the interconversion also proceeds in the direction (IX) ⟶ (VIII).

Quantitative Examination.—In order to avoid sampling, the *whole* of the products obtained in interconversion experiments were transferred to the freezing-point apparatus.

The following f. p.'s are uncorrected, but were determined under identical conditions with the same apparatus. The f. p.'s of artificial mixtures of the isomerides lie on a two-branch curve, the eutectic point of which corresponds to a mixture containing 56·8% of (VIII), having f. p. 113·8°. After determining the f. p.'s of the products of interconversion experiments, a pure isomeride was added and a further f. p. taken in order definitely to locate the corresponding point on the f. p. diagram. It was shown that these

products of the interconversion experiments were strictly binary in character, and that the process of isolation did not introduce impurities affecting the f. p.

F. p.'s of Mixtures of Acids (VIII) *and* (IX).

VIII (%) ...	0·0	16·9	35·0	49·8	60·1	71·5	83·65	100·0
F. p.	169·5°	156·5°	139·0°	122·5°	118·5°	133·5°	148·5°	163·3°

Interconversion of Isomerides.

Acid IX used.	Time (hrs.)	0·0	4·0	8·0	16·0	24·0	48·0		
	F. p.	169·5°	164·0°	156·0°	141·0°	129·0°	129·0°		
	VIII (%)...	0·0	7·5	17·5	33·0	44·0	44·0		
Acid VIII used.	Time (hrs.)	0·0	1·0	2·0	3·5	12·0	16·0	18·0	24·0
	F. p.	163·3°	158·5°	155·5°	149·0°	122·5°	128·5°	129·0°	129·0°
	VIII (%)...	100·0	94·0	90·5	84·0	49·8	44·5	44·0	44·0

Equilibrium : VIII (44·0%) $\rightleftharpoons$ (56·0%) IX.

(3) *Interconversion of Methyl and Ethyl Methoxy-esters.*

Preparation of Esters.—The following esters were obtained both by way of the acid chlorides, which were prepared by means of thionyl chloride, and also by the action of methyl iodide on the appropriate silver salts. *Methyl* α-p-*methoxybenzylcinnamate* is a colourless oil, b. p. 237—238°/14—15 mm., n^{19}_{6563} 1·58904, $n^{19°}_{5893}$ 1·59684, $n^{19°}_{5461}$ 1·60221 (Found : C, 76·7; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). Its isomeride, *methyl* p-*methoxy-α-benzylcinnamate*, b. p. 245°/11—12 mm., solidified and separated from ligroin in rhombic prisms, m. p. 55° (Found : C, 76·7; H, 6·5%). *Ethyl* α-p-*methoxybenzylcinnamate*, a colourless oil, has b. p. 235°/13—14 mm., $n^{23°}_{5893}$ 1·58334, $n^{23°}_{5461}$ 1·58972 (Found : C, 77·0; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·3; H, 6·8%), and the isomeric *ethyl* p-*methoxy-α-benzylcinnamate*, b. p. 240—241°/10—11 mm., separates from ligroin or dilnte alcohol as prismatic needles, m. p. 45° (Found : C, 77·0; H, 6·7%).

Alkaline Hydrolysis of Esters.—After some exploratory work the following method was evolved for use as described subsequently. The ester (1 part) was boiled for 0·5 hour with an aqueous-alcoholic solution of sodium hydroxide prepared from sodium (1 part), methyl or ethyl alcohol (30 parts), and water (22 parts). The acids were isolated as indicated in section (2). The yields and m. p.'s were as follows :

True m. p. of acid.	Ester used.	Yield of acid (unpurified).	M. p. (unpurified).
165·5°	Methyl	98·8%	165·0°
	Ethyl	98·3	165·5
171·5	Methyl	98·4	171·5
	Ethyl	98·4	171·5

These results establish (*a*) that no interconversion of isomerides takes place in the presence of hydroxide ions at 100° under the

B

conditions stated (contrast interconversion by OMe′ and OEt′), (*b*) that, since the yields of acids are constant and almost quantitative, and since no impurities affecting the m. p.'s of the acids are introduced, hydrolysis under the conditions described and subsequent thermal analysis of the acids can be used to follow the interconversion of the esters.

Stability of the Esters to Heat.—Redistillation of the esters and subsequent hydrolysis gave the same results, wherefore it follows that the esters, like the methoxyhydrocarbons, undergo no interconversion on being heated alone to temperatures somewhat above 220°.

Stability of the Methyl Esters to Sodium Methoxide.—The methyl esters (1 part) were boiled, for times up to 24·5 hours, with a solution of sodium methoxide prepared from sodium (1 part) and methyl alcohol (30 parts). Hydrolysis under the conditions described above, followed by f. p. determinations, showed that the esters were entirely unaltered.

Methyl α-*p*-methoxybenzylcinnamate was heated with a similar solution of sodium methoxide at 100° for 72 hours. The f. p. of the acid was 122·0°, and was lowered by addition of *p*-methoxy-α-benzylcinnamic acid. Hence 37% of the ester has been converted into its isomeride. Since, at equilibrium, about 56% is expected to be converted, it is obvious that the catalytic activity of methoxide ions is small.

Interconversion of Ethyl Esters by Sodium Ethoxide.—This was effected at 85° under the conditions used for the methoxy-acids and methoxyhydrocarbons. The approach towards equilibrium from either side was followed by hydrolysis, after addition of the amount of water necessary to produce aqueous-alcoholic sodium hydroxide of the strength stated above, and thermal analysis of the mixture of acids formed. The f. p.'s were taken under the same conditions as those relating to the f. p. data in section (2).

Isomeride used.	Time at 85° with NaOEt (hrs.).	F. p. of acids.	Isomeride X (%).	$k_1 + k_2$ (hour^{-1}).
XI	0·0	169·5°	0·0	—
	8·0	156·5	17·0	0·066
	16·0	150·5	24·5	0·052
	23·0	149·0	26·0	0·051
	72·0	130·5	43·0	—
X	72·0	129·5	44·0	—
	28·0	115·0	56·0	0·054
	16·0	121·0	62·5	0·067
	4·0	152·5	88·0	0·060
	2·0	158·0	93·5	0·059
	0·0	163·3	100·0	—

Equilibrium: X(43·5%) ⇌ (56·5%)XI; velocity coefficient, $k_1 + k_2$ (mean) = 0·0585 hr.$^{-1}$; k_1/k_2 = 0·770; k_1 = 0·0255; k_2 = 0·0330.

We wish to thank the Chemical Society and the Royal Society for grants with the aid of which much of the cost of this investigation has been met.

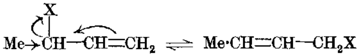
THE UNIVERSITY, LEEDS. [*Received, January 29th*, 1929.]

LXIV.—*Mobile Anion Tautomerism. Part III. A Comparison of the Activation of Three-carbon Anionotropic Systems by Alkyl and by Aryl Groups.*

By HAROLD BURTON.

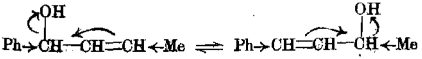
IN Part II (Burton, J., 1928, 1650) it was shown that the activation of the three-carbon anionotropic system (I) Ph·CHX·CH:CH_2 ⟶ Ph·CH:CH·CH_2X (II) by the phenyl group causes a complete conversion of (I) into (II) in suitable solvents. The conditions for the change are dependent on the anionic stability of X (*i.e.*, strengths of acids HX) and also on some molecular property of the solvent closely related to its dielectric constant. The migratory power of X is in the order Br >OAc; O·CO·C_6H_4·NO_2(*p*)>OH.

In the system (III ⇌ IV) the mobility of X is much smaller. For instance, each alcohol yields its own acetyl derivative on boiling

(III.)  (IV.)

with acetic anhydride (Baudrenghien, *Bull. Soc. chim. Belg.*, 1922, **31**, 160; compare Prevost, *Ann. Chim.*, 1928, **10**, 147), and although both alcohols yield the same bromide (α-bromo-Δ^β-butene) (Bouis, *ibid.*, 1928, **9**, 410; Prevost, *loc. cit.*), hydrolysis of this with aqueous alkali carbonate yields 60% of (III) and 40% of (IV). The *p*-nitrobenzoates should resemble the acetates in their stability, and this has been verified for *α-methylallyl* p-*nitrobenzoate* by the author's method (*loc. cit.*) of boiling an acetic anhydride solution for 6 and 24 hours. In each experiment the substance was unchanged.

In consequence of the pronounced difference in activating power of the phenyl and the methyl group a direct comparison of the two was made by examining an anionotropic system terminated at one end by a phenyl and at the other by a methyl group. No difficulty was experienced in the preparation by the usual Grignard method of *α-phenyl-γ-methylallyl alcohol* (V) and the isomeric γ-phenyl-α-methylallyl alcohol (VI) (Klages, *Ber.*, 1902, **35**, 2650).

(V.)  (VI.)

Although it was not possible to prepare a homogeneous *p*-nitrobenzoyl derivative or bromide from either of these alcohols, the alcohol (V) was smoothly and completely converted into the acetate of (VI) by boiling with acetic anhydride. The completeness of the change shows the remarkable property of activating anionotropic systems possessed by the phenyl group. As it also promotes activation in prototropic systems (Ingold and Shoppee, this vol., p. 447), this group is able, by tautomeric electron-displacements of either sign (see Ingold and Shaw, J., 1927, 2918) promoted by the requirements of the system, to absorb an electric charge of either sign produced by the ionisation of an attached atom or group. It is the separation of X as the ion ($X^{\ominus}$) that is the key process, and therefore it follows that the influence (represented by → in III) is probably a *compensating* influence.

From the work of Ingold and others (J., 1927, 997; 1928, 3125) on the decomposition of quaternary ammonium hydroxides it follows that the influence (represented by → in III) of the alkyl group in increasing the toleration of C_α for the shared sextet left by the separation of $X^{\ominus}$ should reach its maximum at about *n*-hexyl. Even then the activation may not be as great as that produced by pheny[l] or by *gem*-dialkyl groups, $\begin{matrix}R'\searrow\\R''\nearrow\end{matrix}C(OH)\cdot CH{:}CH_2$. Compounds of thi[s] structure have been shown (Locquin and Wouseng, *Compt. rend* 1922, **174**, 1711; **175**, 100) to give the derivatives

$$CR'R''{:}CH\cdot CH_2\cdot OAc$$

on acetylation, and the substituted acraldehydes

$$CR'R''{:}CH\cdot CHO$$

on oxidation in acid media. It is hoped to test the action of th[e] *n*-hexyl group on anionotropic systems when some of the exper[i]mental difficulties have been surmounted.

EXPERIMENTAL.

α-*Methylallyl* p-*nitrobenzoate*, $CHMe(O\cdot CO\cdot C_6H_4\cdot NO_2)\cdot CH{:}CH$ was obtained by heating a mixture of methylvinylcarbinol (8·4 g *p*-nitrobenzoyl chloride (23·8 g.), and pyridine (150 c.c.) on t[he] water-bath for 15 hours. The oil which separated when the produ[ct] was poured into water gradually solidified, and the *ester* crystallis[ed] from alcohol in almost colourless needles, m. p. 43—44° (Foun[d]: C, 59·9; H, 4·9. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). Wh[en] the *p*-nitrobenzoate (5 g.) was boiled with acetic anhydride (10 c for 6 and for 24 hours, and the solutions were poured into wat[er,] unchanged material was obtained in each case.

α-*Phenyl*-γ-*methylallyl Alcohol* (V).—The Grignard reagent prepa[red] from magnesium (12 g.), bromobenzene (94 g.), ether (200 c.

and a trace of iodine was cooled below 0°, and a solution of crotonaldehyde (35 g.) in ether (125 c.c.) added during 1·5 hours. The mixture was stirred for a further 4 hours and then decomposed with ice and saturated ammonium chloride solution. The *alcohol* (51 g.; yield, 70%) was obtained from the ethereal extract as a colourless mobile oil, b. p. 121·5—123·5°/14 mm. (Found: C, 80·7; H, 8·05. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%). An attempt to prepare the *p*-nitrobenzoyl derivative in pyridine solution gave an ill-defined solid, m. p. about 60°, which was probably a mixture of *cis*- and *trans*-isomerides and could not be purified by repeated crystallisation from alcohol. The bromide obtained by the action of a 30% solution of hydrogen bromide in glacial acetic acid decomposed on distillation.

γ-Phenyl-α-methylallyl alcohol (VI) was prepared from magnesium methyl iodide and cinnamaldehyde as described by Klages (*loc. cit.*). During the vacuum distillation of the alcohol, small drops of water formed. [This tendency for formation of phenylbutadiene (Straus, *Ber.*, 1909, **42**, 2882) is enhanced by the presence of small amounts of acid substances.] The phenylurethane crystallised from light petroleum or dilute alcohol in clusters of colourless needles, m. p. 92—93° (Klages gives m. p. 94—95°) (Found: C, 76·4; H, 6·4. Calc. for $C_{17}H_{17}O_2N$: C, 76·4; H, 6·4%). Attempts to prepare the *p*-nitrobenzoate and the bromide gave results similar to those obtained with the isomeride.

A prototropic change analogous to Ph·CH(OH)·CH:CH$_2$ ⟶ Ph·CO·CH$_2$·CH$_3$ (Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; see also Burton and Ingold, J., 1928, 908; Shoppee, *ibid.*, p. 2567) is not undergone by either of the above alcohols in presence of 20% lcoholic potassium hydroxide or 5% sodium ethoxide solution.

γ-Phenyl-α-methylallyl Acetate, CHPh:CH·CHMe·OAc.—Either of he alcohols (V) and (VI) (10 g.) was boiled with acetic anhydride 15 c.c.) for 6 hours. The residue obtained after removal of the xcess of acetic anhydride gave on distillation 6·3 g. of the *acetate*,). p. 141—144°/15 mm. (Found: C, 76·3; H, 7·35. $C_{12}H_{14}O_2$ equires C, 75·8; H, 7·4%), together with a dark-coloured, high-oiling residue.

When the acetate was hydrolysed with an excess of 5% sodium thoxide solution, and the product worked up in the usual way, -phenyl-α-methylallyl alcohol, b. p. 130°/11 mm., was obtained: t was further characterised by the m. p. and mixed m. p. of its henylurethane. When a solution of the acetate in chloroform was reated with ozonised oxygen for 36 hours, and the ozonide decomosed by boiling with water for 2—3 hours, no volatile aldehyde Schiff's reagent) was evolved. Benzoic acid, identified by mixed

m. p., separated from the cooled solution. The mother-liquor on evaporation gave a further small quantity of benzoic acid and had a strong odour of pyruvic acid. Pyruvic acid phenylhydrazone, m. p. 185° (decomp.) (compare Bamberger and Grob, *Ber.*, 1901, **34**, 548), was obtained by the action of phenylhydrazine acetate on the residue. The acid was apparently formed by the hydrolysis and further oxidation of the intermediate α-acetoxypropaldehyde.

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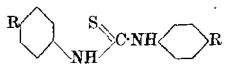
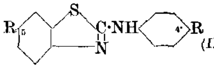
LXV.—*Aminobenzthiazoles. Part XI. The Synthesis of 5 : 4′-Disubstituted 1-Anilinobenzthiazoles from Nuclear-substituted Thiocarbanilides.*

By GEORGE MALCOLM DYSON, ROBERT FERGUS HUNTER, and CHARLES SOYKA.

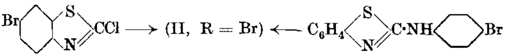
ONE of the original objects of this investigation (J., 1925, **127** 2023), *viz.*, the bromination of di-*p*-substituted *s*-diphenylthio carbamides (I) and of the corresponding 5 : 4′-disubstituted 1-anilino benzthiazoles (II) has now been studied.

(I.)   (II.)

On account of the retarding effect of nuclear bromine on th closure of the thiazole ring (Hunter and Soyka, J., 1926, 2958 the bromination of *s*-di-*p*-bromophenylthiocarbamide (I, R = Br was first examined.

On treatment with bromine in chloroform, this thiocarbamid yielded a *perbromide* which may be a derivative of the hypothetic $(R{\cdot}NH)_2CBr{\cdot}SBr$ addition compound, since it changed into *hydropentabromide* of 5 : 4′-dibromo-1-anilinobenzthiazole when th solution was heated. On reduction, the hydropentabromide yield 5 : 4′-*dibromo*-1-*anilinobenzthiazole* (II, R = Br), which was al prepared by condensation of 1-*chloro*-5-*bromobenzthiazole* (III) wi *p*-bromoaniline, and by decomposition with hydroxylic solven of the bromo-addition compounds obtained by treating 1-anilin

benzthiazole (II, R = H) and *4'-bromo-1-anilinobenzthiazole* (IV) with bromine in chloroform.



(III.) (IV.)

By brominating *s*-di-*p*-chloro- and *s*-di-*p*-fluoro-phenylthiocarbamide, ***hydrotribromides*** of the corresponding dichloro- and difluoro-anilinobenzthiazoles were obtained, and all attempts to prepare higher bromo-addition compounds were unsuccessful. *s*-Di-*p*-carbethoxyphenylthiocarbamide (I, R = CO_2Et), however, gave rise to an unstable ***hydropentabromide*** of ethyl 1-anilinobenzthiazole-5 : 4'-dicarboxylate.

The fact that the hydrotribromides and hydropentabromides can also be prepared by bromination of the hydrobromides of the anilinobenzthiazoles themselves in inert solvents suggests that the compounds are best formulated as polyhalide-ion derivatives (Base, $\overset{+}{H}$) $\overset{-}{Br_3}$ and (Base, $\overset{+}{H}$) $\overset{-}{Br_5}$, analogous to the tribromides and pentabromides of the alkali metals (Wells and Wheeler, *Amer. J. Sci.*, 1892, **43**, 476; Ephraim, *Ber.*, 1917, **50**, 1069) and to the ammonium pentabromide described by Roozeboom (*Ber.*, 1881, **14**, 2398).

In the course of these experiments we were led to re-examine the bromination of acetyldiphenylthiocarbamide. Hugershoff and König (*Ber.*, 1901, **34**, 3136) described the formation of a tribromide, $NPhBr{\cdot}CS(Br_2){\cdot}NPhAc$, which yielded a curiously stable "sulphoxide" on treatment with sulphurous acid; subsequently, Hugershoff (*Ber.*, 1903, **36**, 3121) discovered that the alleged sulphoxide was identical with Hofmann's acetanilidobenzthiazole (*Ber.*, 1879, **12**, 1126; 1880, **13**, 11). The tribromide is actually a *hydrotribromide* of 1-acetanilidobenzthiazole, and the formation of such a compound by an acetyl derivative is worthy of note, arising doubtless from the residual basicity of the nuclear nitrogen atom of the amidine system.

The bromination of the anilinobenzthiazoles themselves in chloroform gives rise to unstable bromo-addition compounds which differ strikingly from the Hugershoff bromides, particularly in the ease with which they change into bromo-substitution derivatives.

The effect of a single nuclear halogen substituent on the bromination of thiocarbanilides was also examined. It was found that *s*-*p*-bromo- and *s*-*p*-chloro-diphenylthiocarbamides,

$$NHPh{\cdot}CS{\cdot}NH{\cdot}C_6H_4X,$$

which might conceivably give rise either to 5-substituted 1-anilinobenzthiazoles or to 4'-substituted derivatives, actually yielded bases

of the latter type (IV), which were identical with those obtained by condensation of 1-chlorobenzthiazole with the corresponding *p*-halogenated anilines.

The tendency of the substituent to seek the *pp'*-positions in 1-anilinobenzthiazole was also observed in cases other than bromination: nitration of this base by fuming nitric acid and iodination by iodine monochloride both produced 5 : 4'-disubstituted 1-anilinobenzthiazoles, identical with those obtained by bromination of the corresponding di-*p*-substituted *s*-diphenylthiocarbamides—observations which suggest that the equivalence of the aromatic nuclei in the *s*-diarylthiocarbamides is partly maintained in the corresponding anilinobenzthiazoles.

EXPERIMENTAL.

5 : 4'-*Dibromo*-1-*anilinobenzthiazole* (II, R = Br).—(A) *Synthesis from* s-*di*-p-*bromophenylthiocarbamide by way of the hydropentabromide, and the isolation of the intermediate perbromide of the thiocarbamide.* A suspension of 2 g. of *s*-di-*p*-bromophenylthiocarbamide in 30 c.c. of chloroform was treated with a solution of bromine (4 c.c.) in the same solvent (4 c.c.), and the mixture heated under reflux on a steam-bath for ½ hour. The perbromide of the thiocarbamide which first separated dissolved, and hydrogen bromide began to be evolved after an inhibition period of some 10 minutes. The *hydropentabromide* crystallised from the hot solution in orange-red needles, which were collected on porous earthenware and dried rapidly in a vacuum for analysis. Because of the instability of the compound, the crystals were kept in the vacuum until the actual moment of weighing [Found: Br (total), 71·8, 71·4, 71·6; Br (labile) (iodometrically in purified acetic acid), 42·5, 42·0; (iodometrically in chloroform containing a few drops of acetic acid), 41·5, 41·0. $C_{13}H_8N_2Br_2S,HBr(Br_4)$ requires Br (total), 71·4; Br (labile), 40·8%]. The hydropentabromide melted with decomposition at 170°, and rapidly lost bromine on exposure to moist air; no lower bromide could, however, be isolated.

The hydropentabromide, suspended in sulphurous acid, was treated with sulphur dioxide until the solid was colourless when crushed. The mixture was basified with ammonia (*d* 0·880) and the product was washed with boiling water and twice recrystallised from alcohol-ethyl acetate, 5 : 4'-*dibromo*-1-*anilinobenzthiazole* being obtained in silky needles, m. p. 221° (Found: N, 7·3; Br, 41·6; S, 8·5. $C_{13}H_8N_2Br_2S$ requires N, 7·3; Br, 41·7; S, 8·3%). The *acetyl* derivative, prepared by boiling a solution of the base in acetic anhydride for a few minutes and diluting the solution with absolute alcohol, separated from alcohol-ethyl acetate in needles, m. p.

205—206° (Found : Br, 37·5. $C_{15}H_{10}ON_2Br_2S$ requires Br, 37·6%). The *hydrobromide*, prepared by saturating a warm suspension of the base in chloroform (0·5 g. in 40 c.c.) with dry hydrogen bromide and concentrating the resulting solution (after filtration) under reduced pressure at laboratory temperature, crystallised in small needles, m. p. 250° (decomp. with charring at 247°), which retained a small quantity of solvent and gave a high value for bromine (Found : Br, 52·9. $C_{13}H_8N_2Br_2S,HBr$ requires Br, 51·6%). Recrystallisation from ethyl acetate and similar solvents led to decomposition into the original components; the hydrobromide was also completely decomposed by cold water, and therefore could not be prepared by concentrating solutions of the dibromo-base in hydrobromic acid, even of *d* 1·45.

By treating a solution of the hydrobromide in chloroform, prepared as described above, with 5 c.c. of bromine and concentrating the resulting solution at 15°/30 mm., orange-red needles of the hydropentabromide were obtained which, after drying, had m. p. 170° (decomp.), alone and when mixed with a specimen prepared by brominating *s*-di-*p*-bromophenylthiocarbamide. The identity was further confirmed by analysis [Found : Br (total), 71·7; Br (labile), 41·5%].

A mixture of 3 g. of *s*-di-*p*-bromophenylthiocarbamide and 3 c.c. of bromine in 50 c.c. of chloroform was well shaken and kept for a short time; the perbromide of the thiocarbamide formed orange needles, m. p. 164° (decomp.) (Found : Br, 71·1%). On treatment of the perbromide with sulphurous acid, the thiocarbamide was regenerated; it was identified by its properties, m. p., and the m. p. of a mixture with a genuine specimen. On treatment with 20% potassium hydroxide solution, the perbromide yielded a product which separated from alcohol–ethyl acetate in colourless flakes, m. p. 275° (decomp. with charring) (Found : Br, 41·3%).

(B) *Synthesis from* p-*bromophenylthiocarbimide by way of* 1-*chloro*-5-*bromobenzthiazole*. A mixture of 30 g. of *p*-bromophenylthiocarbimide (purified by melting on a steam-bath with fused calcium chloride and redistillation under reduced pressure) and 30 g. of phosphorus pentachloride was heated for 30—40 hours in a sealed tube at 170—180°. The product was fractionated under reduced pressure and the fraction, b. p. 157—159°/18 mm., was redistilled. 1-*Chloro*-5-*bromobenzthiazole* formed small white crystals, m. p. 89°, from ether (yield, 0·8 g.) (0·0953 g. gave 0·1280 g. of mixed silver halides. $C_7H_3NClBrS$ requires 0·1270 g.).

A mixture of 0·3 g. of 1-chloro-5-bromobenzthiazole and 0·25 g. of *p*-bromoaniline was gently warmed. Recrystallisation of the product from alcohol–ethyl acetate gave needles of slightly impure

5 : 4′-dibromo-1-anilinobenzthiazole (m. p. 213°, mixed m. p. 218°), from which the pure acetyl derivative (m. p. and mixed m. p. 205—206°) was prepared.

(C) *Synthesis of* 4′-*bromo*-1-*anilinobenzthiazole from* s-*phenyl*-p-*bromophenylthiocarbamide and from* 1-*chlorobenzthiazole and* p-*bromoaniline, and its conversion into the* 5 : 4′-*dibromo-base*. (i) The *hydrotribromide*, m. p. 148° (decomp.) [Found: Br (total), 58·5; Br (labile), 30·0. $C_{13}H_9N_2BrS,HBr(Br_2)$ requires Br (total), 58·6; Br (labile), 29·3%], which crystallised after the solution obtained from 1·3 g. of phenyl-*p*-bromophenylthiocarbamide (in 25 c.c. of chloroform) and bromine (2·5 c.c. in 3 c.c. of chloroform) had been refluxed for 5 minutes, was reduced in the usual way. The 4′-*bromo*-1-*anilinobenzthiazole* separated from alcohol–ethyl acetate in feathery needles, m. p. 214—215° (Found: Br, 26·5; S, 10·2. $C_{13}H_9N_2BrS$ requires Br, 26·2; S, 10·5%). (ii) The condensation of a mixture of 0·3 g. of 1-chlorobenzthiazole with 0·3 g. of *p*-bromoaniline was carried out exactly as described under (B) and the product obtained after basification and recrystallisation was identified with 4′-bromo-1-anilinobenzthiazole by m. p. and mixed m. p. determination.

A suspension of 0·5 g. of 4′-bromo-1-anilinobenzthiazole in 20 c.c. of chloroform was treated with 0·9 c.c. of bromine, the bromo-addition compound which separated from the resulting solution was dissolved in boiling absolute alcohol, and the product obtained by concentrating this solution was basified. The 5 : 4′-dibromo-1-anilinobenzthiazole obtained, after recrystallisation from alcohol–ethyl acetate (animal charcoal), had m. p. 217° and mixed m. p. 219° (acetyl derivative, m. p. 203°, mixed m. p. 204°).

A similar experiment to this with 1·5 g. of 1-anilinobenzthiazole yielded a *hexabromide*, m. p. 140° (Found: Br, 68·3. $C_{13}H_{10}N_2Br_6S$ requires Br, 68·0%), which gave 5 : 4′-dibromo-1-anilinobenzthiazole, m. p. 220°, mixed m. p. 221° (Found: Br, 41·5%), on being dissolved in boiling absolute alcohol.

Hugershoff's dibromoanilinobenzthiazole (*Ber.*, 1903, **36**, 3121) was still ill-defined after several recrystallisations and usually had m. p. 195° (on one occasion a specimen, m. p. 200°, was obtained). It appears to consist mainly of 5 : 4′-dibromo-1-anilinobenzthiazole, since a mixture of the 195° product (Found: Br, 41·0%) with the 5 : 4′-dibromo-base melted at 198—200°. Moreover, the 195° product yielded an acetyl derivative which melted at 191°, and at 199° when mixed with 5 : 4′-dibromo-1-acetanilidobenzthiazole.

Bromination of 5 : 4′-*Dibromo*-1-*anilinobenzthiazole*.—By treatment of the dibromo-base (1·4 g.) in chloroform (25 c.c.) with bromine (2·5 c.c.), an unstable orange *hexabromide* was obtained, m. p. 254° (Found: Br, 73·6. $C_{13}H_8N_2Br_8S$ requires Br, 74·1%). From a

hot absolute alcoholic solution of this, a slightly impure *tetrabromo*-substitution derivative was obtained which separated from alcohol–ethyl acetate in colourless flakes, m. p. 196—198° (Found : Br, 57·7. $C_{13}H_8N_2Br_4S$ requires Br, 59·0%). Attempts to purify this substance further by recrystallisation were unsuccessful.

5 : 4′-*Dichloro*-1-*anilinobenzthiazole* (II, R = Cl).—The *hydrotribromide* separated, during the refluxing of the solution obtained from *s*-di-*p*-chlorophenylthiocarbamide (1·4 g.), chloroform (18 c.c.), and bromine (1·6 c.c.), in orange needles, m. p. 165—167° (decomp.; sintering at 158°) [Found : Br (total), 44·6; Br (labile), 30·0. $C_{13}H_8N_2Cl_2S,HBr(Br_2)$ requires Br (total), 44·8; Br (labile), 29·9%]. This compound, which is remarkably stable, was also produced in all attempts to prepare a hydropentabromide of the dichloroanilinobenzthiazole by using a high concentration of bromine. On reduction, it yielded 5 : 4′-*dichloro*-1-*anilinobenzthiazole*, which separated from alcohol–ethyl acetate in silky white plates, m. p. 224° (Found : N, 9·6; Cl, 23·8; S, 10·6. $C_{13}H_8N_2Cl_2S$ requires N, 9·5; Cl, 24·1; S, 10·85%). The *acetyl* derivative formed needles, m. p. 186—187° (Found : Cl, 21·2. $C_{15}H_{10}ON_2Cl_2S$ requires Cl, 21·1%). The *hydrobromide*, prepared as in the case of the 5 : 4′-dibromo-compound, formed yellowish plates, m. p. 217° (sintering at 212°) (0·1399 g. gave 0·1780 g. of silver halides. $C_{13}H_8N_2Cl_2S,HBr$ requires 0·1771 g.).

The hydrotribromide was also prepared by saturating a suspension of 0·5 g. of the dichloro-base in 40 c.c. of chloroform with hydrogen bromide, adding 5 c.c. of bromine to the solution, and concentrating it under reduced pressure at laboratory temperature. It crystallised in orange needles, which melted at 165—167° alone and when mixed with a specimen of the Hugershoff bromide [0·1278 g. gave 0·2022 g. of silver halides. Calc. 0·2027 g. Found : Br (labile), 29·5%].

By concentrating the solution obtained from 0·25 g. of the dichlorobase and 0·7 c.c. of bromine in chloroform at 15°/30 mm., a *hexabromide* was obtained which crystallised in orange prisms, m. p. 253° (decomp.) (0·1770 g. gave 0·3238 g. of silver halides. $C_{13}H_8N_2Cl_2Br_6S$ requires 0·3233 g.).

Synthesis of 4′-*Chloro*-1-*anilinobenzthiazole from* s-*Phenyl*-p-*chlorophenylthiocarbamide and from* 1-*Chlorobenzthiazole*.—(i) The bromo-addition compound obtained by refluxing a mixture of 1·3 g. of the chlorodiphenylthiocarbamide, chloroform (15 c.c.), and bromine (1·3 c.c.) for 6 minutes and concentrating the solution at 15°/30 mm. crystallised in orange needles, m. p. 130° (decomp.) (0·2238 g. gave 0·3435 g. of silver halides). 4′-*Chloro*-1-*anilinobenzthiazole* separated from alcohol–ethyl acetate in silky needles, m. p. 196° (Found : Cl, 14·0; S, 12·5. $C_{13}H_9N_2ClS$ requires Cl, 13·6; S, 12·3%). (ii) 0·3 G. of 1-chlorobenzthiazole was condensed with *p*-chloro-

aniline as in the previous case. The base obtained had m. p. 198° after recrystallisation and melted at 197° when mixed with the specimen prepared in (i).

5 : 4′-*Di-iodo-1-anilinobenzthiazole*.—(A) On refluxing a mixture of *s*-di-*p*-iodophenylthiocarbamide (1 g.), chloroform (15 c.c.), and bromine (1·5 c.c.), a red bromide separated, m. p. 185°. Concentration of the mother-liquor yielded another bromide, which crystallised in yellow needles, m. p. 211°.

On reduction, both bromides yielded 5 : 4′-*di-iodo-1-anilinobenzthiazole*, which crystallised in glistening needles, m. p. 193° (decomp.), from alcohol–ethyl acetate (Found : I, 53·0; S, 6·9. $C_{13}H_8N_2I_2S$ requires I, 53·1; S, 6·7%).

(B) The 5 : 4′-di-iodo-base was also obtained by treating 1-anilinobenzthiazole (1·5 g.) in glacial acetic acid (15 c.c.) with iodine monochloride (1·5 g.), warming the resulting solution, and diluting it with water (200 c.c.). The product was identified by m. p. and mixed m. p. determination.

5 : 4′-*Difluoro-1-anilinobenzthiazole*.—The solution obtained by refluxing 2 g. of *s*-di-*p*-fluorophenylthiocarbamide, 30 c.c. of chloroform, and 3 c.c. of bromine for 20 minutes was concentrated under reduced pressure; a *hydrotribromide* then crystallised in orange needles, m. p. 150—152° (decomp.; sintering at 148°) [Found: Br (total), 48·0; Br (labile), 32·0. $C_{13}H_8N_2F_2S,HBr(Br_2)$ requires Br (total), 47·7; Br (labile), 31·8%]. This compound was also prepared from the difluoro-base, hydrogen bromide, and bromine in chloroform.

5 : 4′-*Difluoro-1-anilinobenzthiazole* crystallises from methyl alcohol–ethyl acetate in needles, m. p. 227—228° (Found : S, 12·6. $C_{13}H_8N_2F_2S$ requires S, 12·2%). It is much more soluble than the dichloro-, dibromo-, and dicyano-bases in ordinary solvents.

5 : 4′-*Dinitro-1-anilinobenzthiazole*.—(A) The red solid obtained by refluxing 1 g. of *s*-di-*p*-nitrophenylthiocarbamide with bromine (1 c.c.) and chloroform (12 c.c.) was reduced by sulphurous acid. The *dinitro-base* separated from alcohol–ethyl acetate in brilliant yellow plates, m. p. 280° (Found : N, 17·5; S, 10·15. $C_{13}H_8O_4N_4S$ requires N, 17·7; S, 10·1%).

(B) *Nitration of 1-anilinobenzthiazole*. 1 G. of the anilino-base was treated with 5 c.c. of nitric acid (*d* 1·5) at laboratory temperature, a further 5 c.c. of the same acid were then added, and the solution was kept at 15° for an hour. On addition of water (300 c.c.), the dinitro-base was precipitated; after recrystallisation it melted at 280°, alone and when mixed with the specimen already described.

5 : 4′-*Dicyano-1-anilinobenzthiazole*.—The bromo-addition compound obtained from the dicyanodiphenylthiocarbamide (1·6 g.),

chloroform (20 c.c.), and bromine (2 c.c.) crystallised during refluxing in golden plates, m. p. 159—160° (decomp.) (Found: Br, 66·5. $C_{15}H_8N_4Br_6S$,HBr requires Br, 66·9%). The *dicyano-base* separated from alcohol–ethyl acetate in small needles, m. p. 222° (Found: S, 11·2. $C_{15}H_8N_4S$ requires S, 11·6%). On hydrolysis with 25% hydrochloric acid for 30—40 hours, it gave 1-anilinobenzthiazole-5 : 4′-dicarboxylic acid, which was more conveniently prepared from s-di-*p*-carbethoxyphenylthiocarbamide.

Ethyl 1-Anilinobenzthiazole-5 : 4′-dicarboxylate.—The solution obtained by refluxing 1·1 g. of *s*-di-*p*-carbethoxyphenylthiocarbamide, chloroform (18 c.c.), and bromine (1·5 c.c.) for 40 minutes was concentrated under reduced pressure at laboratory temperature; a *hydropentabromide* then separated in small orange crystals, m. p. 110° (decomp.; softening at 97°) [Found: Br (total), 52·6; Br (labile), 44·0. $C_{19}H_{18}O_4N_2S$,HBr(Br_4) requires Br (total), 51·9; Br (labile), 41·5%]. On reduction, *ethyl 1-anilinobenzthiazole-5 : 4′-dicarboxylate* was obtained which, after two recrystallisations from alcohol–ethyl acetate, formed small white plates, m. p. 190—192° (Found: S, 8·8. $C_{19}H_{18}O_4N_2S$ requires S, 8·65%). The analysis of this compound for nitrogen by Dumas's method gave consistently high results due to the formation of methane and we therefore analysed the acid. *Hydrolysis.* The ethyl ester (0·5 g.) was hydrolysed by refluxing it with 50 c.c. of 25% hydrochloric acid for 30—40 minutes. *1-Anilinobenzthiazole-5 : 4′-dicarboxylic acid* formed small white plates from alcohol, which were unmelted at 290° (Found: N, 9·0; S, 10·1. $C_{15}H_{10}O_4N_2S$ requires N, 8·9; S, 10·2%).

Bromination of s-*Di*-p-*anisylthiocarbamide.*—A suspension of 1·3 g. of the dianisylthiocarbamide in chloroform (10 c.c.) was treated with bromine (1·5 c.c.), and the mixture refluxed for 10 minutes. On cooling, brick-red crystals of a bromide separated, m. p. 137° (decomp.) (Found: Br, 62·2%), which yielded a *dibromo-5 : 4′-dimethoxy-1-anilinobenzthiazole*, m. p. 240°, on reduction (Found: Br, 35·9; S, 7·15. $C_{15}H_{12}O_2N_2Br_2S$ requires Br, 36·0; S, 7·2%).

Bromination of Acetyldiphenylthiocarbamide and of 1-Acetanilidobenzthiazole.—(i) The hydrotribromide prepared from 1·2 g. of acetyldiphenylthiocarbamide and bromine (2 c.c.) in chloroform (30 c.c.) crystallised in orange needles, m. p. 167° (decomp.) [Found: Br (total), 47·5; Br (labile), 31·0. Calc. for $C_{15}H_{12}ON_2S$,HBr(Br_2): Br (total), 47·2; Br (labile), 31·4%]. (ii) The hydrotribromide prepared from 1 g. of 1-acetanilidobenzthiazole, 30 c.c. of chloroform, excess of dry hydrogen bromide, and bromine (2·5 c.c.) had the same appearance as the above and melted at 166°, and at 167° when mixed with Hugershoff's compound [Found: Br (total), 47·5; Br (labile),

32·0%]. (iii) Concentration under reduced pressure of the solution obtained from 1 g. of acetanilidobenzthiazole, 20 c.c. of chloroform and 2 c.c. of bromine yielded a *hexabromo-addition compound,* which crystallised in orange needles, m. p. 163° (decomp.) (Found : Br, 63·8. $C_{15}H_{12}ON_2Br_6S$ requires Br, 64·2%).

In conclusion, the authors wish to express their thanks to Professor J. F. Thorpe, F.R.S., for his kind interest in this work, to the Trustees of the Ramsay Memorial Fellowship Trust for the award of a Fellowship to one of them (R. F. H.), and to the Trustees of the Dixon Fund of the University of London for grants which have helped to defray the cost of the materials.

Imperial College of Science and Technology, London, S.W. 7. [*Received, November 14th,* 1928.]

LXVI.—*The Quinoxaline Synthesis : Some Derivatives of 2 : 3-Dimethylquinoxaline.*

By Stanley Thomas Henderson.

The synthesis of 2:3-dimethylquinoxaline from diacetylmonoxime and *o*-phenylenediamine (Gabriel and Sonn, *Ber.*, 1907, **40**, 4850) involves the formation of an intermediate substance, apparently not hitherto recognised as such. The reactions occurring are :

$$C_6H_4(NH_2)_2 + COMe{\cdot}CMe{:}NOH = C_6H_4{<}\begin{matrix}N{:}CMe\\ \vert \\ N{:}CMe\end{matrix} + NH_2{\cdot}OH + H_2O \quad (i)$$

Dimethylquinoxaline (I.)

$$NH_2{\cdot}OH + COMe{\cdot}CMe{:}NOH = HON{:}CMe{\cdot}CMe{:}NOH + H_2O \quad . \quad (ii)$$

$$(I) + HON{:}CMe{\cdot}CMe{:}NOH \rightleftharpoons C_6H_4{<}\begin{matrix}N{=}CMe\\ \vert \\ NH{:}CMe\\ \vert \\ O{\cdot}N{:}CMe{\cdot}CMe{:}NOH\end{matrix} \quad . \quad . \quad (iii)$$

The intermediate (II.)

The *dimethylquinoxaline* derivative (II) of *dimethylglyoxime* is a definite compound which has also been prepared from the constituent base and dioxime; no such combination occurs, however, between dimethylglyoxime and quinoxaline itself, nor will *o*-phenylenediamine condense with the dioxime.

By the action of strong acid or alkali on (II) the base (I) is liberated, as in the normal preparative method (*loc. cit.*). In this method, however, the reactants are used in equimolecular proportion, and the maximum yield of (I) is about 70% on account of loss of diacetylmonoxime by reaction (ii) occurring simultaneously with

(i). The mother-liquor from the preparation, after removal of (I) by steam distillation in excess of alkali, consequently contains unattacked diamine which will react with more monoxime. It is evident that complete utilisation of the diamine can only be attained by adding 2 mols. of monoxime per mol. of diamine. Actually a 90% yield was thus obtained.

From 2 : 3-dimethylnaphthaquinoxaline a similar *compound* is formed, having two molecules of the base combined with one molecule of dimethylglyoxime.

Bromination of dimethylquinoxaline or of (II) in alcoholic solution gives *5 : 6 : 7 : 8-tetrabromo-2 : 3-dimethylquinoxaline*, which has very feebly basic properties and considerable stability.

EXPERIMENTAL.

The Intermediate (II).—*o*-Phenylenediamine (1 mol.) in warm aqueous solution containing acetic acid (2 mols.) was treated slowly with a warm aqueous solution of diacetylmonoxime (1 mol.), whereby a mass of orange needle-shaped crystals was soon produced. This intermediate *substance* (II) was separated from the deep brown liquid and recrystallised from alcohol: more was obtained by further addition of the monoxime (1 mol.) to the mother-liquor.

Steam distillation of the original acid liquid with (II) in suspension slowly produced (I), but after addition of excess of alkali to the reaction liquid the base could be rapidly removed by this means or by extraction with ether. Acidification after removal of the base precipitated dimethylglyoxime.

The substance (II), on repeated crystallisation, formed lemon-yellow flakes, m. p. 182°. It also melted at 182° when mixed with the colourless product formed from dimethylglyoxime and dimethylquinoxaline in alcoholic solution. The "salts" prepared by the two different methods were of identical microscopic appearance. The temperature 182° was quite definite, but was only the *initial* m. p., the substance becoming completely liquid at about 215°. The initial m. p. was unaltered when the substance was mixed with dimethylglyoxime (m. p. 245°), but dimethylquinoxaline (m. p. 104°) lowered it to 103°: (II) evidently dissociates on heating (Found: C, 61·5, 61·6; H, 6·6, 6·7; N, 20·2, 20·4; *M*, by Rast's camphor method, 151. $C_{14}H_{18}O_2N_4$ requires C, 61·3; H, 6·6; N, 20·4%; *M*, 274).

The substance (II) is insoluble in ether, ligroin, benzene, and chloroform and only slightly soluble in water. It is converted by the action of concentrated hydrochloric acid into diacetyl and a salt of dimethylquinoxaline, and by alkali into the base itself. In

alcoholic solution it shows as sensitive a colour reaction as dimethylglyoxime with nickel salts. A solution of (II) was used to estimate nickel by the usual procedure : the weights of precipitate obtained in two experiments were 0·1822 and 0·1832 g. Dimethylglyoxime gave 0·1809 and 0·1810 g. from the same quantity of nickel solution.

2 : 3-*Dimethylnaphthaquinoxaline*.—Equal weights (3 g.) of 1 : 2-naphthylenediamine and diacetylmonoxime, mixed in warm aqueous-alcoholic solution, produced an oil which soon crystallised in orange needles. Recrystallised from alcohol, these became lighter in colour. Melting began at 123° and was complete at about 200°. The nickel reaction was observed as above (Found : C, 72·0; H, 6·0; N, 15·6. $C_{32}H_{32}O_2N_6$ requires C, 72·1; H, 6·1; N, 15·8%). The base, liberated by alkali, extracted with ether, and recrystallised from dilute alcohol, was pale yellow and melted at 101—102°. It combined with dimethylglyoxime to give the same intermediate "salt," initial m. p. 122°.

5 : 6 : 7 : 8-*Tetrabromo*-2 : 3-*dimethylquinoxaline*. — Dimethylquinoxaline (or the intermediate II), brominated in alcoholic solution on a water-bath with excess of bromine, gave a crystalline mass. After being washed with alcohol and water and recrystallised from absolute alcohol, glacial acetic acid, or benzene, the pale pink or colourless *substance* melted at 234° (decomp.). It was insoluble in water or ether, dissolved in concentrated sulphuric or nitric acid, and was reprecipitated unchanged on dilution several hours later. It was not appreciably attacked by boiling chromic and glacial acetic acids or by alkaline permanganate. Bromine was not removed by aqueous alkali or boiling alcoholic silver nitrate, but a mixture of chromic and sulphuric acids acted violently on the substance, bromine being evolved (Found : C, 25·5; H, 1·3; Br, 67·6. $C_{10}H_6N_2Br_4$ requires C, 25·3; H, 1·3; Br, 67·5%).

Bromination of dimethylquinoxaline in chloroform solution gave the above substance, but the chief product was another faintly coloured substance, m. p. 150° after four recrystallisations from dilute alcohol. The bromine in this substance was partly removed by hot aqueous alkali (Found : Br, 51·6. $C_6H_8N_2Br_2$ requires Br, 50·6%).

The author is greatly indebted to Dr. W. H. Mills, F.R.S., for constant help and advice during the work of which the above is a part.

NORTHWICH, CHESHIRE. [*Received, January 15th, 1929.*]

LXVII.—*The Influence of Substituents on the Reimer–Tiemann Reaction.*

By Herbert Henry Hodgson and Thomas Alfred Jenkinson.

In the usual recipes for the production of hydroxybenzaldehydes from phenol, the ratio of *o*- to *p*-hydroxybenzaldehyde actually isolable is given as 4—5 : 1, but since the authors' experience with *m*-halogenophenols (*J.*, 1927, 1740, 3041) was that this ratio was nearer unity, it appeared of interest to widen the scope of the inquiry. Accordingly, a standardised reaction has been conducted with a number of phenols, the resulting aldehydes being estimated by two methods depending upon isolation of their *p*-nitrophenylhydrazones (compare Hodgson and Beard, *J. Soc. Chem. Ind.*, 1926, **45**, 56T). The results were as follows :

Initial phenol.	Ortho/para ratio. Method (*a*).	Ortho/para ratio. Method (*b*).	Initial phenol.	Ortho/para ratio. Method (*a*).	Ortho/para ratio. Method (*b*).
Phenol	0·72	0·6	*m*-Chlorophenol	0·79	0·71
o-Cresol	0·56	0·48	*m*-Bromophenol	0·94	0·72
m-Cresol	0·52	0·46	*m*-Iodophenol ...	0·94	0·78
o-Chlorophenol	2·1	1·6			

Although these ratios can only be regarded as approximate, consideration of those given by method (*b*), which are regarded as the more accurate, leads to the following conclusions :

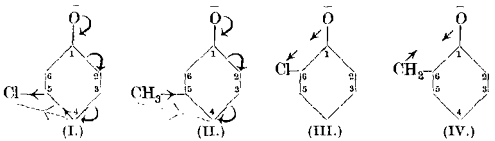
(1) Under Reimer–Tiemann conditions, the para-position in phenol itself is found to be more reactive than the ortho (o/p = 0·6). Since activity is due to the charged phenoxide ion, the observed result appears to be in accordance with current electronic theory, alternating (tautomeric) effects reaching the para- more easily than the ortho-positions (Ingold, *Ann. Reports*, 1926, **23**, 141).

(2) The influence of chlorine in the 5-position may be explained from two points of view : (i) If it exerted its usual $p > o$ directing effect, superposed on the $p > o$ directing effect of the phenoxide ion, the o/p ratio (0·71) would tend towards unity. (ii) If it exerted its combined general (direct) and inductive effects (see Allan, Oxford, Robinson, and Smith, J., 1926, 401 ; Baker and Ingold, J., 1927, 832 ; Cooper and Ingold, *ibid.*, p. 836) [see (I)], the 4-position would be deactivated more than the 2-position, with the resultant increase of the o/p ratio (0·6 to 0·71).

(3) That the second view is probably the more correct would appear to follow from the results with *m*-cresol (II), where the o/p ratio (0·46) has been still further diminished (from 0·6) by the direct and inductive effects (*loc. cit.*) of the methyl group.

(4) The unusual reactivity of the 2- compared with the 4-position

in 6-chlorophenol (o/p = 1·6) appears to be best explained on the assumption that the positive field (general effect) of the chlorine



(I.) (II.) (III.) (IV.)

atom attracts the negative field of the oxygen atom sufficiently to relieve the 2-position of a considerable amount of the steric hindrance due to the oxygen atom (III), whilst with *o*-cresol (IV) the exact opposite occurs, *i.e.*, the repulsion produced on the oxygen field by the negative methyl group field increases the steric hindrance effect on 2-position (o/p = 0·48). This view would appear to be supported by the established abnormal behaviour of *o*-chlorophenol in other respects (compare Sidgwick and Turner, J., 1922, **121**, 2260).

(5) The results with *m*-bromo- and *m*-iodo-phenol agree, even though slightly, with the accepted deactivation order Cl>Br>I.

EXPERIMENTAL.

Method.—The particular phenol (0·05 mol.) was dissolved in a solution of sodium hydroxide (10 g.) in water (40 c.c.) and treated with chloroform (20 g.) at one addition, the mixture being gently refluxed for 2 hours. The reaction product was worked up in two ways:

(*a*) After addition of hydrochloric acid until just acid, the unchanged phenol, chloroform, and *o*-hydroxy-aldehyde were removed by steam distillation, 600—900 c.c. of distillate being necessary according to the phenol used. The oil was separated, dissolved in glacial acetic acid, and treated at 70° with an excess of *p*-nitrophenylhydrazine hydrochloride in the same solvent, this mixture being subsequently added to the aqueous portion of the distillate. The resulting *p*-nitrophenylhydrazone was dried at 80—90° and weighed. After removal of excess of *p*-nitrophenylhydrazine by means of acetone, the unused phenol was estimated by precipitation as bromo-compound. The liquor containing the non-volatile *p*-hydroxyaldehyde was filtered, the tar extracted six times with boiling water (50 c.c.), and the combined liquor treated with excess of an aqueous solution of *p*-nitrophenylhydrazine hydrochloride, the hydrazine being estimated as above.

(*b*) The entire reaction mixture was dissolved in glacial acetic acid, a little water being added subsequently to keep sodium acetate

solution. The filtered solution was then divided into two equal portions, one of which was steam distilled and estimated as under (*a*), the other having its total aldehyde content determined as a mixture of *p*-nitrophenylhydrazones. The data given above represent the mean values of six determinations for each phenol. In all cases examined, the unchanged phenol was approximately half the amount initially taken, only small quantities of resinous matter and condensation products being formed, which do not appreciably affect the *o*/*p* ratio. Variations up to 5 hours in the time of conducting the Reimer–Tiemann reaction had a negligible effect on the yields of substituted aldehydes and on their ratio, but acidification of the alkaline reaction product by mineral acid appeared to reduce the measurable yield of *p*-hydroxyaldehyde in all cases investigated. The actual loss of *p*-hydroxybenzaldehyde in practice would appear to be consequent on the method of isolation adopted.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December 13th,* 1928.]

LXVIII.—*Diphenylaminearsinic Acids. Part I. Derivatives of Diphenylamine-4-arsinic Acid.*

By HARRY JAMES BARBER.

INVESTIGATIONS of the relation between trypanocidal action and chemical constitution have resulted in an exhaustive study of the effects of substitution in a single aromatic nucleus containing an arsenic group, and to a less extent in arsenic derivatives containing more than one aromatic nucleus.

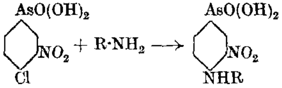
Derivatives in which other substituted aromatic nuclei are attached to that containing the arsenic group by linkages of the types ·CO·NH· and ·NH·CO·NH· are numerous, but those involving a closer union, such as diphenylamine, have not been extensively studied.

The reactivity of the various chloronitrophenylarsinic acids in which the chlorine is in the ortho- or the para-position with respect to the nitro-group suggested the use of these for the preparation of considerable quantities of certain types of diphenylamines. Since this paper is restricted to the consideration of diphenylamine-4-arsinic acids, only the reactions of 4-chloro-3-nitrophenylarsinic acids will be discussed here, but the reactions of the other chloronitrophenylarsinic acids mentioned are being investigated.

The reactivity of the chlorine atom is shown by its replacement by NH_2, NHMe, NMe_2, and $NH{\cdot}CH_2{\cdot}CO_2H$ groups when the arsinic acid

is heated in aqueous media with the corresponding amine (D.-R.P. 285,604, 412,171, 446,545). It also reacts with piperidine (King, J., 1927, 1053) and with ethylenediamine and piperazine (Fourneau and Funke, *Bull. Soc. chim.*, 1928, **43**, 889).

It was found that 4-chloro-3-nitrophenylarsinic acid reacted very readily with most aromatic amines when an aqueous solution of its sodium salt was warmed with a suspension or solution of the amine at 95° for several hours. The products obtained by using aniline, 4-aminophenol, 4-aminoacetanilide, 4-amino-2-acetamidophenol, or anthranilic acid are described here, but *o*-chloroaniline, *o*-toluidine, and sulphanilic acid have also been found to condense; the nitro-anilines are apparently not sufficiently basic to react under the conditions employed.



[R = C_6H_5, C_6H_4·OH, C_6H_4·NHAc, C_6H_3(OH)·NHAc, or C_6H_4·CO_2H.]

The 2-nitrodiphenylamine-4-arsinic acids thus obtained were reduced to the corresponding amino-compounds, and certain derivatives were also prepared. The biological results, for which I am indebted to Mr. J. G. Everett, B.Sc., A.I.C., of this laboratory, are summarised in the following table.

The tolerated dose (*T*) was determined by intravenous injection in normal mice, and the curative dose (*C*) on mice infected with *Trypanosoma equiperdum*; both are expressed as mg./g. of mouse. The period of observation was 7 days. For comparison, 3-amino-4-piperidinophenylarsinic acid (King, *loc. cit.*), 3-amino-4-piperazinophenylarsinic acid (Fourneau and Funke, *loc. cit.*), and 3 : 4-diaminophenylarsinic acid are included.

Arsinic acids.	*T*.	*C*.	*C*/*T*.
3 : 4-Diaminophenylarsinic acid	2·0	0·15	1/13
3-Amino-4-piperidinophenylarsinic acid	<0·1	>0·1	—
3-Amino-4-piperazinophenylarsinic acid	0·5	>0·5	—
2-Aminodiphenylamine-4-arsinic acid	0·05	0·05	1
2-Acetamidodiphenylamine-4-arsinic acid	0·1	0·1	1
2-*iso*Propylideneaminodiphenylamine-4-arsinic acid (or *N*-phenyl-2 : 2-dimethyl-2 : 3-dihydrobenziminazole)	0·1	>0·1	—
2 : 4′-Diaminodiphenylamine-4-arsinic acid	0·1	0·1	1
2-Amino-4′-acetamidodiphenylamine-4-arsinic acid	0·6	0·1	1/6
2 : 4′-Diacetamidodiphenylamine-4-arsinic acid	2·0	—	—
2-Amino-4′-hydroxydiphenylamine-4-arsinic acid	0·5	0·25	1/2
2-Amino-3′-acetamido-4′-hydroxydiphenylamine-4-arsinic acid	1·0	>1·0	—
Arsenobenzenes (administered orally).			
3 : 3′-Diamino-4 : 4′-dianilinoarsenobenzene	>10·0	0·5	<1/20
3 : 3′-Diamino-4 : 4′-di-*p*-acetamidoanilinoarsenobenzene	>10·0	1·0	<1/10

In this series of compounds the introduction of an unsubstituted phenyl group in the 4-amino-group of 3 : 4-diaminophenylarsinic acid results in a very marked increase in toxicity, despite the lower arsenic content, and somewhat greater trypanocidal effect; this unexpected and interesting discovery is being further investigated. Substitution in the non-arsenated phenyl nucleus results in modification of the toxicity and curative action, which follows, in general, that of similar substitution in phenylarsinic acid. As is usual, the introduction of an acetyl group in the amino-group results in a decrease of both toxicity and curative action.

EXPERIMENTAL.

4-Chloro-3-nitrophenylarsinic acid (D.-R.P. 245,536) is prepared by nitration of 4-chlorophenylarsinic acid, obtained by a modification of the Bart reaction from *p*-chloroaniline, but as precise details of the nitration are not given, the preparation is described here.

To 4-chlorophenylarsinic acid (24 g.) dissolved in concentrated sulphuric acid (70 c.c.), nitric acid (*d* 1·52; 7·5 c.c.) was added without cooling. The mixture was heated on a water-bath for 1 hour and poured on ice, and the arsinic acid separated; yield, 24 g. (85%). Nitration does not occur at 0°, and despite the statement (D.-R.P. 285,604) that 4-chloro-3 : 5-dinitrophenylarsinic acid is prepared by " energetic nitration," no trace of this has been obtained even under the most drastic conditions. The acid crystallises from hot water in diamond plates (Found : As, 27·0. Calc. for $C_6H_5O_5NClAs$: As, 26·7%); the calcium salt crystallises in needles and the barium salt in plates.

2-*Nitrodiphenylamine*-4-*arsinic Acid*.—The foregoing acid (28 g.), dissolved in 2*N*-caustic soda (50 c.c.) and water (150 c.c.), was heated for 16—20 hours on a steam-bath with aniline (10 g.; 5% excess of 2 mols.). Part of the required acid crystallised, and the remainder was obtained by acidification (Congo red) with hydrochloric acid. The yield was almost quantitative but the crude material was contaminated by aniline. The crude acid was converted into the sodium salt in concentrated aqueous solution; this was salted out with sodium chloride and dissolved in a large volume of water, the solution was heated to boiling in the presence of charcoal and filtered, and the *acid* precipitated hot with hydrochloric acid. It separated in fine yellow needles (Found : As, 21·9, 22·0; N, 8·5. $C_{12}H_{11}O_5N_2As$ requires As, 22·2; N, 8·3%), sparingly soluble in boiling water, almost insoluble in cold. It is somewhat more soluble in dilute and readily soluble in hot glacial acetic acid.

2-*Aminodiphenylamine*-4-*arsinic Acid*.—The 2-nitro-acid was re-

duced with ferrous hydroxide at 80—90° by the method of Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1581). The crude amino-acid (80% yield) crystallised with a purple colour, which could only be removed by dissolving the acid in sodium hydroxide solution, adding a *trace* of sodium hydrosulphite, boiling the solution with charcoal, filtering it, and acidifying it with acetic acid. The pure *acid* crystallises from hot water in white rectangular plates (Found: As, 24·6; N, 9·4. $C_{12}H_{13}O_3N_2As$ requires As, 24·3; N, 9·1%), which rapidly turn blue on exposure to air; m. p. 170—175° with preliminary darkening.

The *monohydrochloride* forms long slender needles from 2*N*-hydrochloric acid which are readily hydrolysed by water and slowly lose hydrogen chloride in air (Found: As, 22·6; Cl, 9·0. $C_{12}H_{13}O_3N_2As,HCl$ requires As, 21·8; Cl, 10·3%).

On attempting to recrystallise the base from hot acetone, a condensation product was obtained containing acetone, not driven off at 100° but readily lost on warming with dilute acid or alkali; this was either 2-*iso*propylideneaminodiphenylamine-4-arsinic acid or *N*-phenyl-2 : 2-dimethyl-2 : 3-dihydrobenziminazole (Found: As 21·5, 21·7; N, 7·5, 7·6; $COMe_2$, 14·3, 14·6. $C_{15}H_{17}O_3N_2As$ require As, 21·5; N, 8·05; $COMe_2$, 16·2%). Treatment of the base wit nitrous acid gives quantitatively N-*phenylbenztriazole-5-arsinic aci* (Found: As, 23·4; N, 12·7. $C_{12}H_{10}O_3N_3As$ requires As, 23·5; N 13·15%).

2-*Acetamidodiphenylamine-4-arsinic acid*, obtained by acetylatic of the amino-derivative in alkaline solution with acetic anhydrid crystallises from alcohol in small diamond-shaped plates (Founc As, 21·8; N, 7·85. $C_{14}H_{15}O_4N_2As$ requires As, 21·5; N, 8·0%). (being boiled (5 g.) with 2*N*-hydrochloric acid (50 c.c.), it giv N-*phenyl-2-methylbenziminazole*-5(6)-*arsinic acid* (compare *J.* *Chem.*, 1904, **69**, 40) (Found: As, 22·6. $C_{14}H_{13}O_3N_2As$ requires A 22·6%).

2-*Nitro-4'-hydroxydiphenylamine-4-arsinic acid*, prepared by t condensation of 4-chloro-3-nitrophenylarsinic acid with *p*-ami phenol exactly as described for aniline (above), crystallises fr alcohol in reddish-brown needles (Found: As, 20·5; N, 8 $C_{12}H_{11}O_6N_2As$ requires As, 21·2; N, 7·9%).

2-*Amino-4'-hydroxydiphenylamine-4-arsinic acid*, obtained reduction with ferrous hydroxide in the usual way, crystallises fr very dilute acetic acid in grey flat needles, which are very suscepti to atmospheric oxidation (Found: As, 22·9; N, 8·4. $C_{12}H_{13}O_4N$ requires As, 23·1; N, 8·65%). *4'-Hydroxy-1-phenyl-1 : 2 : 3-be triazole-5-arsinic acid* crystallises in colourless needles (Found: 22·5; N, 12·4. $C_{12}H_{10}O_4N_3As$ requires As, 22·4; N, 12·5%).

2-*Nitro-4′-acetamidodiphenylamine-4-arsinic acid*, from *p*-aminoacetanilide and 4-chloro-3-nitrophenylarsinic acid, crystallises in faintly red needles (Found : As, 18·75. $C_{14}H_{14}O_6N_3As$ requires As, 19·0%).

2-*Amino-4′-acetamidodiphenylamine-4-arsinic acid* forms irregular flat needles (Found : As, 20·7. $C_{14}H_{16}O_4N_3As$ requires As, 20·5%). Acetylation gives 2 : 4′-*diacetamidodiphenylamine-4-arsinic acid* (Found : As, 18·6. $C_{16}H_{18}O_5N_3As$ requires As, 18·4%), which crystallises in fine colourless needles from dilute acetic acid.

2 : 4′-*Diaminodiphenylamine-4-arsinic acid*, prepared by boiling the 4′-acetyl compound (5 g.) with 2*N*-sulphuric acid (50 c.c.) for 3 hours, forms long slender prisms (Found : As, 23·6. $C_{12}H_{14}O_3N_3As$ requires As, 23·2%).

2-*Nitro-3′-acetamido-4′-hydroxydiphenylamine-4-arsinic acid* forms fine yellow needles from hot water (Found : As, 18·7. $C_{14}H_{14}O_7N_3As$ requires As, 18·7%).

2-*Amino-3′-acetamido-4′-hydroxydiphenylamine-4-arsinic acid* crystallises in fine colourless needles from 50% acetic acid (Found : As, 19·9. $C_{14}H_{16}O_5N_3As$ requires As, 20·2%).

2′-*Carboxy-2-nitrodiphenylamine-4-arsinic acid* forms yellow needles from hot 50% acetic acid (Found : As, 20·1. $C_{13}H_{11}O_7N_2As$ requires As, 19·6%).

Nitration of 2-Acetamidodiphenylamine-4-arsinic Acid.—Owing to the failure to condense *o*- and *p*-nitroanilines with 4-chloro-3-nitrophenylarsinic acid, the direct nitration of 2-acetamidodiphenylamine-4-arsinic acid was carried out in the hope of obtaining the 2′- or 4′-nitro-derivative, which on reduction would give 2′- or 4′-amino-2-acetamidodiphenylamine-4-arsinic acid isomeric with the 2-amino-4′-acetamido-compound described above, but it was not possible to obtain a mononitro-derivative, for dinitration occurred even at −10° with only 1 mol. of nitric acid or potassium nitrate.

2′ : 4′(?)-*Dinitro-2-acetamidodiphenylamine-4-arsinic acid* crystallises from 50% acetic acid in clusters of fine yellow needles (Found : As, 16·9, 17·2; N, 12·5. $C_{14}H_{13}O_8N_4As$ requires As, 17·0; N, 12·7%). A satisfactory method of orienting this product has not yet been found.

The two arseno-compounds mentioned in the table (p. 472) were prepared from the arsinic acids by reduction with sodium hydrosulphite in the usual way. They are both yellow amorphous powders, which oxidise rapidly in air and are soluble in excess of hydrochloric acid : 3 : 3′-*diamino-4 : 4′-dianilinoarsenobenzene* (Found : As, 28·2. $C_{24}H_{22}N_4As_2$ requires As, 29·1%); 3 : 3′-*diamino-4 : 4′-di-p-acetamidoanilinoarsenobenzene* (Found : As, 23·8. $C_{28}H_{28}O_2N_6As_2$ requires As, 23·8%).

In conclusion, I wish to record my thanks to Dr. A. J. Ewins for his kindly criticism of this paper, and to Mr. R. H. Klein, F.I.C., for the analytical results.

RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD.,
WANDSWORTH, S.W. 18. [Received, December 29th, 1928.]

LXIX.—*The Nitration of* m-*Acetamido*-tert.-*butylbenzene.*

By JOHN BALDWIN SHOESMITH and ALEXANDER MACKIE.

GELZER (*Ber.*, 1888, **21**, 2949) was the first to nitrate *m*-acetamido-*tert.*-butylbenzene and claimed to have isolated 2-nitro-3-acetamido-*tert.*-butylbenzene as the sole reaction product. The constitution of this compound was determined as follows. On hydrolysis it yielded the corresponding nitroamine, which when reduced gave a diamino-*tert.*-butylbenzene of m. p. 109°, and this readily condensed with phenanthraquinone to give a phenanthra-*tert.*-butylphenazine (compound A), m. p. 144°. In a parallel series of experiments with *p*-acetamido-*tert.*-butylbenzene, the phenazine obtained, m. p 146·5°, was considered by Gelzer to be different from compound A and since the nitration of *p*-acetamido-*tert.*-butylbenzene was known to give 3-nitro-4-acetamido-*tert.*-butylbenzene the composition o the nitration product from *m*-acetamido-*tert.*-butylbenzene was a stated above.

In view of the difficulty with which the position ortho to the *tert* butyl group in *tert.*-butylbenzene is attacked (J., 1928, 2334) Gelzer observation appeared remarkable, since it requires direct attack of position which is ortho to both substituent groups in *m*-acetamid *tert.*-butylbenzene. The nitration of *m*-acetamido-*tert.*-buty benzene has now been repeated, the nitroamine obtained hydrolysis of the reaction product reduced, and the diamine co densed with phenanthraquinone. The resulting phenazine has be found to have m. p. 148·5—149° and to be identical in all respe with that obtained from 3 : 4-diamino-*tert.*-butylbenzene prepar from 3-nitro-4-amino-*tert.*-butylbenzene. This result proves th the nitration of *m*-acetamido-*tert.*-butylbenzene takes place expected in position 4, and it is interesting to note the differe between this nitration and that of aceto-*m*-toluidide, which nitrated predominantly in the 6-position. The reluctance of group to enter the ortho-position to a *tert.*-butyl group in te butylbenzene is again apparent.

EXPERIMENTAL.

The compounds described in Gelzer's paper as derivatives of *iso*-*butylbenzene* are in reality derived from *tert*.-butylbenzene.

*4-Nitro-3-amino-*tert.*-butylbenzene.*—*m*-Acetamido-*tert*.-butylbenzene (Shoesmith and Mackie, *loc. cit.*, p. 2338) was added to vigorously agitated nitric acid (*d* 1·46) at 25—30° during 15 minutes; the mixture was then poured into a large excess of ice-water. The nitro-compound crystallised from alcohol in pale yellow needles, m. p. 116° (Gelzer, *loc. cit.*, gives m. p. 105·5°) (Found: N, 12·1. Calc.: N, 11·9%); yield, 41%. When hydrolysed with alcoholic potassium hydroxide, it gave 4-nitro-3-amino-*tert*.-butylbenzene, which crystallised from alcohol in yellow leaflets, m. p. 91—92° (Gelzer gives 124°) (Found: N, 14·1. Calc.: N, 14·4%); yield, 81%.

*Phenanthra-*tert.*-butylphenazine.*—The above nitroamine (3 g.) was dissolved in warm concentrated hydrochloric acid, the calculated quantity of stannous chloride added, and the whole vigorously agitated. The resulting solution was cooled, freed from tin by the addition of zinc, and decanted from the metal, and a large excess of concentrated aqueous sodium hydroxide added. The liberated diamine, isolated by means of ether, was obtained as a light brown solid which crystallised from water in micaceous colourless leaflets, rapidly darkening in the air and of m. p. 97—98°. The diamine in alcoholic solution, when added to the calculated quantity of phenanthraquinone in glacial acetic acid, gave the phenazine as a mass of pale yellow, interlaced needles; these recrystallised from aqueous alcohol in very small, yellow needles, m. p. 148·5—149° (Gelzer gives 144°). It was more satisfactory to proceed to the phenazine in this way than to attempt to purify the diamine completely, as there was present a very small quantity of impurity which was removable with great difficulty from the diamine, whereas there was no difficulty in purifying the phenazine.

In order to characterise this compound, 3-nitro-4-amino-*tert*.-butylbenzene, prepared by the nitration of *p*-acetamido-*tert*.-butylbenzene and subsequent hydrolysis, was reduced to the diamine, which was condensed with phenanthraquinone as before. The phenazine obtained had m. p. 148·5—149·5° (Gelzer gives 146·5°) and was identical in all respects with that obtained from the nitrated *m*-acetamido-*tert*.-butylbenzene; a mixture of the two compounds melted at 148—149°.

The authors wish to state that the investigation was completed during the tenure of a teaching fellowship awarded to one of them (J. B. S.) by the Carnegie Trustees.

EDINBURGH UNIVERSITY. [*Received, January 23rd, 1929.*]

LXX.—*The Action of Semicarbazide Hydrochloride and of 2 : 4-Dinitrophenylhydrazine Hydrochloride on Aldoximes and their Derivatives.*

By Oscar L. Brady and Frank Herbert Peakin.

Knöpfer (*Monatsh.*, 1910, **31**, 87) showed that the reaction

$$\text{R·CH:N·NHPh} + \text{H}_2\text{N·NH·CO·NH}_2\text{,HCl} \rightleftharpoons \text{R·CH:N·NH·CO·NH}_2 + \text{NHPh·NH}_2\text{,HCl}$$

was a balanced one and that by using an excess of semicarbazide hydrochloride it was possible to convert phenylhydrazones into semicarbazones, and *vice versa.*

When an aldoxime in solution is treated at room temperature with a solution of an equivalent amount of semicarbazide hydrochloride, it is slowly converted into the semicarbazone: this, being much less soluble than the oxime, crystallises and the conversion is almost complete. It was thought possible that this replacement might lead to the production of stereoisomeric semicarbazones when stereoisomeric oximes were employed, but both the α- and the β-forms of *p*-methoxy-, *m*-nitro-, and *p*-nitro-benzaldoximes gave the same semicarbazones: search was made for small quantities of isomeric compounds, but without success. No reaction occurred when aldoximes were treated with a solution of semicarbazide itself. Apparently, therefore, the formation of the semicarbazone is preceded by hydrolysis of the oxime to the aldehyde; if this is so, the production of stereoisomeric semicarbazones would not be expected. As would be anticipated from their greater ease of hydrolysis, the *N*-methyl derivatives of the above oximes reacted more rapidly than the oximes with semicarbazide hydrochloride, giving the semicarbazones. *O*-Methylbenzaldoxime was only slowly transformed into the semicarbazone.

The following experiment typifies the method employed. A solution of α-*m*-nitrobenzaldoxime (1·6 g.) in alcohol (5 c.c.) was treated at room temperature with a solution of semicarbazide hydrochloride (1·1 g.) in water (2 c.c.). A precipitate appeared after 30 minutes, 0·7 g. of semicarbazone had separated after 12 hours, and a further 0·15 g. after 2 days. Both products were identical with *m*-nitrobenzaldehydesemicarbazone, m. p. (rapidly heated) 244°, prepared from the aldehyde. The addition of water to the mother-liquor precipitated more semicarbazone of the same melting point.

A solution of 2 : 4-dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid (Brady and Elsmie, *Analyst*, 1926, 77) reacts

somewhat readily at room temperature with aldoximes and their derivatives, giving practically quantitative yields of the crystalline 2 : 4-dinitrophenylhydrazones of the corresponding aldehydes. Owing to the sparing solubility and non-volatility of these compounds the reaction provides a method for the quantitative determination of small quantities of oximes.

The following experiments indicate the scope of the method. (1) *α*-*p*-Nitrobenzaldoxime (0·1707 g.) was dissolved in alcohol (5 c.c.) and to this was added a solution of 2 : 4-dinitrophenylhydrazine hydrochloride (250 c.c.) in 2*N*-hydrochloric acid containing 1 g. of base per litre. The mixture was kept with occasional shaking for 24 hours and the precipitated *p*-nitrobenzaldehydedinitrophenylhydrazone was then collected in a Gooch crucible, washed with 2*N*-hydrochloric acid and with water, and dried at 100° to constant weight. The yield of dinitrophenylhydrazone (0·3194 g.) corresponded to 93·5% of the oxime taken. (2) Similarly, *N*-methyl-*o*-methoxybenzaldoxime (0·1055 g.) in water (10 c.c.) gave dinitrophenylhydrazone (0·2018 g.) corresponding to 99·9% of the compound taken. (3) A saturated aqueous solution of *o*-methoxybenzaldoxime at 18° was found by this method to contain 0·868 g. per litre. A direct determination by extraction with ether and weighing gave 0·880 g.

Although *O*-methylbenzaldoxime can be hydrolysed only with difficulty by acids and is unusually unreactive, yet on shaking with a solution of 2 : 4-dinitrophenylhydrazine hydrochloride and keeping for 2 days it is quantitatively converted into benzaldehydedinitrophenylhydrazone, from which benzaldehyde can he obtained by warming with moderately concentrated sulphuric acid. This is the easiest method of recovering the aldehyde from the *O*-methyl derivative of the oxime.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 4th*, 1920.]

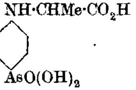
LXXI.—*Compounds of the Tryparsamide Type. Part I. Resolution of* N-*Phenylalanine-4-arsinic Acid and of its Amide.*

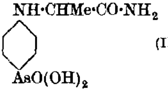
By CHARLES STANLEY GIBSON, JOHN DOBNEY ANDREW JOHNSON, and BARNETT LEVIN.

N-PHENYLGLYCINEAMIDE-4-ARSINIC acid ("tryparsamide") was first prepared by Jacobs and Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1589) and, along with numerous derivatives, examined

therapeutically by (Miss) Pearce and Brown (*J. Exp. Med.*, 1921, **33**, 193). Tryparsamide has been described as the most effective organic arsenical for the treatment of human sleeping sickness due to infection by *Tr. gambiense.*

In attempting to extend our knowledge of organic arsenicals belonging to this series, it was decided to investigate in the first place those externally compensated compounds which can be resolved into their optically active components, so that the therapeutic value of the optical isomerides might be compared as well as that of the externally compensated compound itself. Further, it is hoped to ascertain whether the marked differences in pharmacological and therapeutical action found among other analogous groups of optical isomerides exist in this series also (compare Cushny, "Biological Relations of Optically Active Substances," 1926).*

(I.) 

 (II.)

dl-N-*Phenylalanine*-4-*arsinic acid* (I) was prepared by the condensation of sodium *p*-arsanilate ("atoxyl") with α-bromopropionic acid in aqueous solution (compare D.-R.P. 204,664 of 1908; Meister, Lucius, and Brüning), and preliminary investigation indicates that it has some therapeutic value. It is essentially a dibasic acid, although titration against sodium hydroxide and phenolphthalein indicates a slightly greater basicity than two in dilute solutions. The *methyl* and the *ethyl* ester—only the carboxyl group being esterified—of the acid were prepared, and from the former, but not from the latter, the corresponding amide-acid, *dl*-*N*-phenylalanineamide-4-arsinic acid (II), was obtained by the action of aqueous ammonia. This amide-acid has been prepared by Jacobs and Heidelberger [*loc. cit.*, p. 1597; who name it *N*-(phenyl-4-arsonic acid)-α-amino-propionamide] and by Fourneau and Nicolitch (*loc. cit.*, p. 1211) by the action of α-bromopropionamide on *p*-arsanilic acid. The decomposition point of this *dl*-amide-acid recorded by Jacobs and Heidelberger (darkening at 255° and decomposing at

* The present work was begun some two years ago. It was almost completed when Fourneau and Nicolitch announced the successful resolution of *dl*-*N*-phenylalanineamide-4-arsinic acid (phenylmethylglycineamidearsinic acid) and the application of the optically active enantiomorphs to the resolution of synthetic ephedrine. In correspondence, M. Fourneau encouraged us to continue our work and sent us a copy of the thesis of M. Nicolitch. This has since been published (Fourneau and Nicolitch, *Bull. Soc. chim.* 1928, **34** 1232).

262—263·5°) is somewhat higher than that recorded by us (never higher than 244°), but too much stress should not be laid on this, since the actual temperature at which the profound decomposition sets in has been found to depend almost entirely on the rate of heating and it is not easy to record the same decomposition point on identical specimens.

The resolution of *dl-N*-phenylalanine-4-arsinic acid was effected in aqueous solution, 2 mols. of the dibasic acid, 2 mols. of sodium hydroxide, and 2 mols. of brucine being used. The *normal brucine salt* of the *d*-acid separated under the conditions described on p. 484 and was optically pure after one recrystallisation from aqueous solution. From this pure brucine salt the pure d-*acid* was easily isolated. The pure l-*acid* was obtained by crystallising three times from water the crude acid liberated from the mother-liquor from which the above brucine salt had been removed, the optically active acids being appreciably less soluble in water than the *dl*-acid. The optically active *monoethyl* and *monomethyl esters* were prepared, their rotatory powers being of the same sign as those of the optically active acids from which they were obtained. They have very much higher melting and decomposition points than the inactive esters and their lower solubility, especially of the methyl esters in water, is very marked. The corresponding amide-acids were made by dissolving the optically active methyl esters in aqueous ammonia: their rotatory powers were of opposite sign to those of the esters (and of the optically active acids) from which they were prepared.

When a solution of the monosodium salt of the optically active amide-acid was boiled with an excess of sodium hydroxide until ammonia ceased to be evolved, the rotatory power of the remaining aqueous solution was of the opposite sign to that of the amide-acid taken, but it was very much lower in value than that of the sodium salt of the pure acid in equivalent concentration. This was confirmed in the case of both isomerides, and it was evident that considerable racemisation had taken place during the cycle of operations *d*-dibasic acid ⟶ *d*-methyl ester ⟶ *d*-amide-acid (*lævo*rotatory) ⟶ *d*-dibasic acid.

There was no evidence in the experimental work to indicate that racemisation had taken place during the conversion of the optically active acid into the corresponding methyl ester: the latter only needed to be freed from mechanical impurities (one crystallisation) to be optically pure. It was possible, however, that some racemisation had occurred during amide-acid formation (compare Wren, J., **1909**, **95**, 1596) and possibly also during the hydrolysis of the amide-acid.

The pure optically active amide-acids were prepared by the resolution of *dl-N*-phenylalanineamide-4-arsinic acid, which was easily effected in aqueous solution with 2 mols. of the amide-acid and 1 mol. each of sodium hydroxide and quinine under the conditions described in the experimental portion. The quinine salt of the *l*-amide-acid needed only one crystallisation from water for complete purification, and from this pure quinine salt the pure *l*-amide-acid was isolated. The pure *d*-amide-acid was obtained by recrystallising three times from water the crude *d*-amide-acid isolated from the mother-liquor from the above quinine salt of the *l*-amide-acid. This method of resolution of the *dl*-amide-acid is somewhat different from that employed by Fourneau and Nicolitch, who used equimolecular quantities of the *dl*-amide-acid and quinine and appear to have had greater difficulties than have been encountered in the present work in obtaining the pure optically active amide-acids. Attempted resolutions, using the half-molecule method, with brucine and strychnine were unsuccessful; in the latter case a crystalline strychnine salt was obtained, but this proved to be a partial racemate.

These optically pure amide-acids had distinctly higher rotatory powers than those obtained from the optically active methyl esters by the action of ammonia. When the pure *l*-amide-acid (*dextro*-rotatory) was hydrolysed by boiling its aqueous solution with an excess of sodium hydroxide until ammonia ceased to be evolved, the resulting solution was *lævo*rotatory and the rotatory power was very much lower than that of the pure *lævorotatory* dibasic acid in equivalent concentration. This proved that in the above cycle of operations racemisation takes place, not only during the conversion of the optically active methyl ester into the optically active amide-acid of the opposite sign, but also during the hydrolysis of the optically active amide-acid to the optically active dibasic acid, again of the opposite sign.

Since the *dextro*rotatory dibasic acid has been proved to be the parent substance of the *lævo*rotatory amide-acid, it seems advisable to adopt Fischer's system of nomenclature for configuration and sign of rotation. The above cycle of operations is therefore more completely expressed as follows :

D. *d*-Dibasic acid ⟶ D. *d*-Ester acid

racemisation) ↖ ↙ (racemisation)

D. *l*-Amide-acid

The following is a résumé of the optical rotation constants ($[\alpha]_{5461}$) of the pure compounds described in the present communication :

Brucine salt of D. *d*-dibasic acid (water)	− 10·61°	
Quinine salt of D. *l*-amide-acid (water)	−123·8	
	Dextro.	Laevo.
N-Phenylalanine-4-arsinic acid (disodium salt, water)	+ 56·40°	− 55·94°
N-Phenylalanine-4-arsinic acid (ethyl ester) (alcohol)	+127·9	−125·8
N-Phenylalanine-4-arsinic acid (ethyl ester) (sodium salt, water)	+103·0	−102·8
N-Phenylalanine-4-arsinic acid (methyl ester) (*sodium salt, water*)	+176·6	−116·3
N-Phenylalanineamide-4-arsinic acid (sodium salt, water)	− 17·88	+ 16·47

EXPERIMENTAL.

dl-N-*Phenylalanine*-4-*arsinic Acid* (I).—A solution of α-bromopropionic acid (35 g.) in water (38 c.c.) was added to a hot solution of sodium *p*-aminophenylarsinate ("atoxyl" or "soamin" containing $5H_2O$; 50 g.) in water (165 c.c.), and the mixture boiled for 8 hours. The product crystallised in somewhat yellowish needles when the resulting solution was kept for 16—40 hours in the ice-chest. dl-N-*Phenylalanine*-4-*arsinic acid*, recrystallised from a large volume of boiling water, decolorising charcoal being used to remove the small amount of colour, formed colourless needles, decomp. 207—210°. 16·75 G. were consistently obtained in every preparation (Found: As, 25·9, 26·1. $C_9H_{12}O_5NAs$ requires As, 25·9%).

The acid is soluble to the extent of about 0·5% in cold water and about 6% in boiling water. It dissolves readily in dilute mineral acids and in acetic acid; it is readily soluble in hot methyl and ethyl alcohols and moderately easily soluble in the cold solvents. It is also slightly soluble in acetone, but insoluble in benzene and ether. In aqueous solution it reduces ammoniacal silver nitrate, a silver mirror being produced, and thus behaves similarly to *o*- and *p*-tolylglycines (Staats and Ehrlich, *Ber.*, 1883, **16**, 204; Cosack, *ibid.*, 1880, **13**, 1091). The acid itself behaves on titration as slightly more than a dibasic acid (phenolphthalein); the end-point is, however, not well defined and varies with the dilution.

Ethyl Ester of dl-N-*Phenylalanine*-4-*arsinic Acid.*—A mixture of the preceding acid (5·0 g.), absolute ethyl alcohol (30 c.c.), and concentrated sulphuric acid (0·5 c.c.) was boiled for 2 hours and poured into water (100 c.c.). The *ethyl* ester, which separated on standing, crystallised from dilute ethyl alcohol (30%) in colourless, doubly-refracting prisms, m. p. 175—177° (decomp.) (Found: As, 23·6. $C_{11}H_{16}O_5NAs$ requires As, 23·6%). The ester is readily soluble in ethyl alcohol and in hot water and behaves on titration as a slightly more than monobasic acid (phenolphthalein), the end-point not being sharply defined.

Methyl ester of dl-N-*phenylalanine*-4-*arsinic acid* was prepared in an

analogous manner to the ethyl ester, pure methyl alcohol being used. After distillation of some 50% of the excess of alcohol, the reaction product was poured into a cold saturated aqueous solution of ammonium sulphate. The separated ester, containing a little ammonium sulphate, was completely extracted with pure methyl alcohol, the methyl alcohol distilled off, and the residue crystallised from the minimum quantity of hot water. It was obtained in colourless acicular needles, m. p. 181° (slight decomp.); yield, 70% (Found: As, 24·3. $C_{10}H_{14}O_5NAs$ requires As, 24·75%). This methyl ester is distinctly more soluble than the ethyl ester.

dl-N-*Phenylalanineamide-4-arsinic Acid* (II).—This amide was prepared in two ways:

(*a*) The methyl ester (4 g.) was added gradually to an aqueous solution of ammonia (*d* 0·880; 12 c.c.), cooled in ice. It dissolved fairly readily, and the solution was kept at the ordinary temperature for 48 hours, the excess of ammonia then being removed by leaving the mixture over sulphuric acid under reduced pressure. The residue, a thick gum, was stirred with a little water, and the amide precipitated by the addition of a slight excess of acetic acid. The product crystallised from boiling water in colourless needles, m. p. 233—240° (decomp.) (Found: N, 9·5; As, 25·5. Calc. for $C_9H_{13}O_4N_2As$: N, 9·7; As, 26·0%).

(*b*) α-Bromopropionamide (70 g.) was boiled with a solution of "atoxyl" or "soamin" (containing $5H_2O$; 115 g.) in water (325 c.c.) for 1 hour. The method of working up the product was similar to that described by Fourneau and Nicolitch (*loc. cit.*, p. 1241); 75 g. were obtained, m. p. 244° (decomp.) (Found: N, 9·4%) (compare Jacobs and Heidelberger, *loc. cit.*).

Attempted Reduction of dl-N-*Phenylalanine-4-arsinic Acid*.—Reduction of the arsinic acid with sodium hydrosulphite, with or without magnesium chloride, gave a yellow material, soluble in alkaline solutions, which contained much sulphur but too little arsenic for an arseno-compound. Reduction of a saturated solution of the acid in concentrated hydrochloric acid containing a trace of hydriodic acid at a low temperature with sulphur dioxide gave a crystalline product which could not be isolated on account of its ready solubility in the mixture at the ordinary temperature.

Resolution of dl-N-*Phenylalanine-4-arsinic Acid*.—To a boiling solution of the acid (70 g.) in 0·516*N*-sodium hydroxide (469·5 c.c.) and water (565·5 c.c.), brucine (113 g.) was added and the boiling was continued until almost the whole had dissolved. Crystallisation began almost immediately, and, after standing at the ordinary temperature for 16 hours, the crystalline material was filtered off, washed with a little water, and recrystallised from 2 litres of boiling

water. After one further recrystallisation under similar conditions, its rotatory power * in aqueous solution was constant: $c = 1{\cdot}1446$, $l = 4$, $\alpha = -0{\cdot}48°$, whence $[\alpha] = -10{\cdot}61°$. The *brucine* salt of *l*-*N*-phenylalanine-4-arsinic acid crystallises from water in large colourless plates containing $7H_2O$ (Found for air-dried material: H_2O, 10·6; N, 6·0. $C_9H_{12}O_5NAs,2C_{23}H_{26}O_4N_2,7H_2O$ requires H_2O, 10·5; N, 5·8%. Found for anhydrous material: As, 6·9. $C_9H_{12}O_5NAs,2C_{23}H_{26}O_4N_2$ requires As, 6·9%).

d- *and* l-N-*Phenylalanine*-4-*arsinic Acids*.—To obtain the d-*acid*, the above brucine salt was ground three times with small quantities of a concentrated aqueous solution of ammonia, the brucine filtered off, and the filtrate extracted thoroughly with chloroform to remove any dissolved brucine. The aqueous solution after evaporation on the water-bath to about 100 c.c. was acidified with hydrochloric acid (Congo red), and the precipitated acid filtered off from the cold mixture. After one recrystallisation from water its rotatory power was constant and it was obtained in colourless needles, m. p. 220—221° (decomp.) (Found: As, 26·0. $C_9H_{12}O_5NAs$ requires As, 25·9%). For its rotatory power determination, the acid was treated with the calculated quantity of a standard aqueous solution of sodium bicarbonate to form the normal salt, and this solution made up to volume with water: $c = 0{\cdot}8562$, $l = 4$, $\alpha = +1{\cdot}93°$, whence $[\alpha] = +56{\cdot}40°$.

The l-*acid* was isolated from the mother-liquor remaining after the separation of the above brucine salt of the *d*-acid. The solution was made alkaline with aqueous ammonia, the brucine filtered off, and the solution extracted thoroughly with chloroform and evaporated to small bulk on the water-bath. The *l*-acid was precipitated with hydrochloric acid and after three crystallisations from water its rotatory power was constant. It resembled the *l*-acid in appearance and had the same decomposition point (Found: As, 25·6%). As in the case of the *d*-acid, its rotatory power was determined in aqueous solution containing exactly sufficient sodium bicarbonate to form the disodium salt: $c = 0{\cdot}8942$, $l = 4$, $\alpha = -2{\cdot}00°$, whence $[\alpha] = -55{\cdot}94°$.

15·5 G. of the pure *d*-acid and 10·0 g. of the pure *l*-acid were obtained. The partly resolved acid recovered on working up the mother-liquors was submitted to further resolution, the quantities of brucine, etc., employed being adjusted in accordance with the rotatory power of the partly resolved acid.

Ethyl Esters of d- *and* l-N-*Phenylalanine*-4-*arsinic Acids*.—These were prepared from the corresponding optically active acids by the

* All rotatory power determinations were carried out at 20° with the mercury-green ($\lambda = 5461$) line.

method used for the preparation of the ethyl ester of the *dl*-acid. Being somewhat less soluble, they are even more easily obtained. In appearance they resemble the *dl*-ester, but their decomposition point is very much higher, 275—276° [Found: (for the d-*ester* prepared from the *d*-acid) As, 23·5; (for the l-*ester* prepared from the *l*-acid) As, 23·75. $C_{11}H_{16}O_5NAs$ requires As, 23·6%].

The following rotatory power determinations were made in pure ethyl-alcoholic solutions :

d-ester : $c = 0{\cdot}4464$, $l = 4$, $\alpha = +2{\cdot}28°$, whence $[\alpha] = +127{\cdot}9°$.
l-ester : $c = 0{\cdot}7132$, $l = 4$, $\alpha = -3{\cdot}59°$, whence $[\alpha] = -125{\cdot}8°$.

The following rotatory power determinations were made in aqueous solutions containing the exact quantity of sodium bicarbonate to form the sodium salt :

d-ester : $c = 0{\cdot}4118$, $l = 4$, $\alpha = +1{\cdot}70°$, whence $[\alpha] = +103{\cdot}0°$.
l-ester : $c = 0{\cdot}3960$, $l = 4$, $\alpha = -1{\cdot}63°$, whence $[\alpha] = -102{\cdot}8°$.

Methyl Esters of d- *and* l-N-*Phenylalanine*-4-*arsinic Acids*.—These were made in a similar manner to the methyl ester of *dl*-*N*-phenylalanine-4-arsinic acid. A preliminary experiment indicated that the optically active ester is very much less soluble in water than the optically inactive one; the esterification mixture therefore was poured into water instead of into a saturated solution of ammonium sulphate. After one recrystallisation from water the esters were optically pure, a yield of over 90% being obtained. The two esters crystallised in long colourless needles, m. p. 277—278° (decomp.). They are very sparingly soluble in water and are conveniently recrystallised from boiling water (6 g. to 200 c.c.) [Found: (d-*ester*) As, 25·1; (l-*ester*) As, 24·6. $C_{10}H_{14}O_5NAs$ requires As, 24·75%]. The rotatory power determinations were done in aqueous solutions containing the calculated quantity of sodium bicarbonate to form the sodium salt :

d-ester : $c = 0{\cdot}6194$, $l = 4$, $\alpha = +2{\cdot}92°$, whence $[\alpha] = +117{\cdot}6°$.
l-ester : $c = 0{\cdot}4982$, $l = 4$, $\alpha = -2{\cdot}32°$, whence $[\alpha] = -116{\cdot}3°$.

Each of these optically active methyl esters was converted int the corresponding optically active amide-acid under precisely th same conditions as those employed in the preparation of the *dl* amide-acid from the *dl*-methyl ester. In each case the product wa recrystallised once from water and obtained in colourless needle m. p. 242—243° (decomp.) [Found: (amide-acid from *d*-meth ester) N, 9·9; (amide-acid from *l*-methyl ester) N, 9·6. Calc. fc $C_9H_{13}O_4N_2As$: N, 9·7%].

The rotatory powers were determined in aqueous solution co

taining the exact quantity of sodium bicarbonate to form the sodium salt :

(*a*) Amide-acid from *d*-methyl ester : $c = 0{\cdot}6114$, $l = 4$, $\alpha = -0{\cdot}33°$, whence $[\alpha] = -13{\cdot}3°$.

(*b*) Amide-acid from *l*-methyl ester : $c = 0{\cdot}6536$, $l = 4$, $\alpha = +0{\cdot}36°$, whence $[\alpha] = +13{\cdot}9°$.

The solution used in (*a*) (40 c.c.) was treated with sodium hydroxide (1 g. in 2 c.c. of water) and boiled for 10 minutes; ammonia then ceased to be evolved. The resulting solntion was cooled and made up to 50 c.c., and its rotatory power determined. It had $[\alpha] = +26{\cdot}6°$. The solution used in (*b*) (40 c.c.) was treated in an exactly similar manner and the final rotatory power was $[\alpha] = -29{\cdot}5°$.

Resolution of dl-*Phenylalanineamide-4-arsinic Acid.*—The amide-acid was prepared by the method described by Jacobs and Heidelberger (*loc. cit.*; compare Fourneau and Nicolitch, *loc. cit.*). The amide-acid (36 g.) was dissolved in boiling water (2000 c.c.) and aqueous sodium hydroxide (0·516*N*; 121 c.c.), and quinine (22·3 g., allowing 10% excess on account of water content) added. The whole was brought into solution and allowed to cool during 20 hours. The salt crystallised in soft needles, and was separated from the mother-liquor. The salt was recrystallised from boiling water (2000 c.c.), and another recrystallisation from water (1500 c.c.) failed to affect the rotatory power. The salt was anhydrous (Found : N, 9·1; As, 12·2. Calc. for $C_9H_{13}O_4N_2As,C_{20}H_{24}O_2N_2$: N, 9·15; As, 12·3%). The rotatory power was determined in aqueous solution : $c = 0{\cdot}2412$, $l = 4$, $\alpha = -1{\cdot}20°$, whence $[\alpha] = -123{\cdot}8°$.

l- *and* d-N-*Phenylalanineamide-4-arsinic Acids.*—The above quinine salt was decomposed by grinding with aqueous ammonia (*d* 0·880), and the liquid filtered. The separated quinine was re-extracted twice with further quantities of ammonia solution. The filtrate was acidified with concentrated hydrochloric acid (Congo red), and the precipitated amide-acid recrystallised from boiling water (decolorising charcoal); its rotatory power was then constant. The pure *l*-amide-acid crystallised in colourless needles, m. p. 247° (decomp.) (Found : N, 9·4. Calc. for $C_9H_{13}O_4N_2As$: N, 9·7%). Its rotatory power was determined in aqueous solution containing the exact quantity of sodium bicarbonate to form the sodium salt : $c = 0{\cdot}5868$, $l = 4$, $\alpha = -0{\cdot}42°$, whence $[\alpha] = -17{\cdot}88°$.

The mother-liquor after separation of the above salt was evaporated to about half its original volume, and the quinine precipitated by addition of a slight excess of an aqueous solution of ammonia.

After filtration, the liquid was acidified with concentrated hydrochloric acid (Congo red), and the amide-acid precipitated as before. This was recrystallised three times from boiling water; its rotatory power was then constant. In appearance and general behaviour the pure *d*-amide acid was similar to its enantiomorphous isomeride and it had the same melting-decomposition point (247°) (Found : N, 9·5%). Its rotatory power was determined as in the previous case : $c = 0{\cdot}7770$, $l = 4$, $\alpha = +0{\cdot}51°$, whence $[\alpha] = +16{\cdot}5°$.

Before the effect of hydrolysis on these pure optically active amide-acids was examined, the rotatory power of another specimen of the pure *d*-amide-acid was determined under the same conditions as the above : $c = 0{\cdot}7050$, $l = 4$, $\alpha = +0{\cdot}46°$, whence $[\alpha] = +16{\cdot}4°$.

This solution (40 c.c.) was treated in an exactly similar way to those in the previous experiments on the hydrolysis of the optically active amide-acids : the rotatory power of the final solution was $[\alpha] = -28{\cdot}5°$.

The authors wish to express their grateful thanks to the Government Grant Committee of the Royal Society and to Messrs. Imperial Chemical Industries Ltd. for grants which have been of great assistance in the purchase of chemicals and apparatus. One of them (B. L.) is indebted to the Department of Scientific and Industrial Research for a grant which enabled him to take part in the work.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E. 1. [*Received, January 25th*, 1929.]

LXXII.—*The Ternary System Mercuric Chloride–Mercuric Iodide–Water.*

By RUTH SUGDEN.

BOULLAY (*Ann. Chim. Phys.*, 1827, **34**, 340) and Larocque (*J. Phar Chim.*, 1843, **4**, 15) describe the formation of a compound $HgCl_2$,Hg which Köhler (*Ber.*, 1879, **12**, 1188) considered he had obtained a yellow solid after boiling the iodide in water with excess of chlor for 12 hours. From a study of the melting-point curves of binary system, Padoa and Tibaldi (*Atti R. Accad. Lincei*, 19 [v], **12**, ii, 158) concluded that there existed a discontinuous se of mixed crystals but no chloroiodide. There has evidently b some difficulty in interpreting results, and this appears to be partly to the fact that, as with the pure iodide, the stability of solids obtained changes with temperature. An indication of nature of the binary system may, however, be gained from

following observations on the ternary system at 30° and 70°, which have been made at the suggestion of Professor A. C. D. Rivett. The two salts have been found to be mutually soluble but, at the iodide end, two series of mixed crystals, yellow and red, respectively, are obtainable, their relative stabilities depending upon temperature and chloride content. They correspond to the yellow and the red form of the simple iodide stable above and below 129° (Reinders, *Z. physikal. Chem.*, 1900, **32**, 507). As chloride progressively dissolves in the yellow iodide, products are obtained which are stable at temperatures below this transition point.

EXPERIMENTAL.

The system was examined at 30° and 70°. The procedure adopted in preparing complexes was to heat suitable mixtures of the components to 100° and then rapidly to filter the solution from any excess solid. The filtrate was rotated for many hours (in some cases up to 11 days) in a closed glass tube in a thermostat at the required temperature, solid separating out. Unless one starts thus from a homogeneous system, trustworthy results cannot be obtained, since equilibrium throughout solids present from the beginning is established far too slowly. As, however, the solubility of the iodide is not much affected by temperature, the amount of solid obtained at the iodide end of the system by the practice adopted was usually very small, especially at 70°, and the accuracy of analysis was correspondingly diminished. After equilibrium had been attained, wet solid was separated as rapidly as possible on a heated Gooch crucible, transferred to a stoppered weighing bottle, and weighed. Both this and the saturated solution were then analysed.

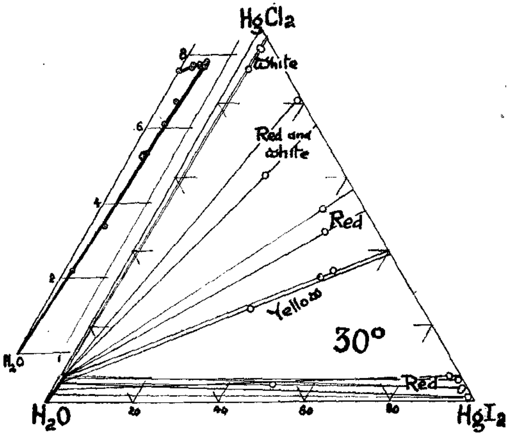
For purposes of analysis, the solid was brought into solution by addition of the minimum amount of potassium iodide. Ammonium sulphate, in amount equal to at least 1% of the weight of the solution, was added to ensure coagulation of mercuric sulphide, which was then precipitated by hydrogen sulphide under pressure. The sulphide was filtered off and washed on a Gooch crucible, dried at 105—110°, and weighed. From the filtrate, the excess gas was removed by boiling, and iodine set free by addition of sodium nitrite and sulphuric acid. The iodine was removed by boiling, and the chloride in the solution determined gravimetrically as silver chloride. The iodide was thus determined by difference, an unsatisfactory procedure when its amount was relatively small. In such cases it was found better to determine it gravimetrically as silver iodide in a solution which was just sufficiently ammoniacal to prevent the precipitation of the chloride. In a system of such

small solubilities and with these obvious limitations in analytical accuracy, the results have qualitative rather than quantitative significance.

Table I(*a*) gives the results at 30°, compositions being expressed as percentages by weight. Water (not recorded) is obtainable by difference. The colours of the mixed crystals are denoted by letters.

There are two solution curves, as may be seen in Fig. 1. The white solids corresponding to the shorter curve (see large-scale portion) are mercuric chloride containing a few parts of iodide per

Fig. 1.



cent. The points shown on the second curve probably belong to two distinct curves which lie very closely together, the corresponding solids being red and yellow mixed crystals of iodide containing chloride. The accuracy obtainable by the present method of working does not permit one to separate these curves. As judged by the time for which yellow crystals may be kept, it seems probable that at 30° the yellow solid is unstable throughout relatively to the red, but at 70° (Table I*b*) the former becomes the stable phase in those solutions in which the concentration of mercuric chloride is greatest.

There is no evidence of compound formation.

TABLE I.

Solutions (Percentages, by weight)		Wet solids			Solutions (Percentages, by weight)		Wet solids		
$HgCl_2$.	HgI_2.	$HgCl_2$.	HgI_2.		$HgCl_2$.	HgI_2.	$HgCl_2$.	HgI_2.	
(a) *System at* 30°.									
7·55	—	—	—	W	6·75	0·31	5·8	93·6	R
7·67	0·41	89·0	2·5	,,	6·14	0·37	2·81	95·7	,,
7·67	0·25	94·7	2·5	,,	5·32	0·28	4·5	50·4	,,
7·75	0·21	94·2	2·7	,,	5·26	0·28	1·23	98·0	,,
7·76	0·38	80·6	18·3	W & R	3·39	0·33	7·0	90·6	,,
7·78	0·49	60·5	21·0	,,	2·20	0·18	—	97·7	,,
7·78	0·52	45·5	42·1	R	7·82	0·52	33·3	47·4	Y
7·72	0·54	51·9	38·4	,,	7·85	0·57	34·9	49·8	,,
7·69	0·46	3·5	95·2	,,	5·36	0·37	24·7	34·6	,,
(b) *System at* 70°.									
19·12	—	—	—	W	12·8	0·99	—	—	Y
19·5	0·44	82·8	1·62	,,	12·6	0·94	12·1	84·6	,,
20·5	1·10	30·9	64·7	Y	10·2	0·91	11·2	62·0	Y & R
19·8	1·02	—	—	,,	9·9	0·84	9·7	87·0	,,
17·4	0·99	20·2	76·0	,,	7·35	0·75	17·2	74·7	R
16·7	1·00	—	—	,,	3·94	0·52	—	—	,,

W = White; R = red; Y = yellow.

UNIVERSITY OF MELBOURNE. [*Received, January 14th,* 1929.]

LXXIII.—*Orientation Effects in the Diphenyl Series. Part VII. The Effect of Substituents in One Nucleus on the Ratio of Ortho : Para Nitration in the Other. The Nitration of 2- and 4-Nitro- and of 2 : 4- and 2 : 4′-Dinitro-diphenyl and of Diphenyl-4-carboxylic Acid.*

By HERBERT CHARLES GULL and EUSTACE EBENEZER TURNER.

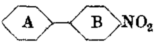
IT was recently pointed out (Le Fèvre and Turner, J., 1928, 245) that the then-known facts, *viz.*, the semi-quantitative results of Bell and Kenyon (J., 1926, 2705), in connexion with the nitration of 2- and 4-nitrodiphenyl indicated that the two nuclei of diphenyl are independently conjugated. These two compounds have now been nitrated quantitatively. 4-Nitrodiphenyl is nitrated to the extent of 37% and 63% in the 2′- and the 4′-position respectively, and 2-nitrodiphenyl gives 39% of the 2′-nitro- and 61% of the 4′-nitro-compound. In neither case is 2 : 4-dinitrodiphenyl formed, nor, we think, would its formation be expected (compare, however, Bell and Kenyon, *loc. cit.*, for the converse opinion) in view of the known retarding influence of a nitro-group on further substitution

in the same nucleus. More important is the proof of the non-formation of detectable quantities of 3′-nitro-derivatives.

From the point of view of establishing the independence of the two nuclei, the nitration of 2 : 4-*dinitrodiphenyl*, hitherto unknown, is even more pertinent. This substance has been obtained by heating a mixture of iodobenzene and 1-chloro-2 : 4-dinitrobenzene with copper bronze (the first example, as far as we are aware, of the synthesis of an unsymmetrical diphenyl derivative by the Ullmann reaction), and has been found to be nitrated to the extent of 45% in position 2′ and 55% in position 4′, less than 1% of a third product being formed, a fact which clearly demonstrates the nuclear independence referred to above.

Since distortion of the diphenyl molecule such as leads to optical activity does not appear, so far as is known at present, until the 2 : 2′ : 6 : 6′-positions are crowded, the 2′/4′ ratio (corresponding to the *o*/*p* ratio in simple benzene substitution) for the nitration of *2-nitrodiphenyl should not be materially different from that of the 4-isomeride in so far as this ratio is determined by purely steric effects. This is in agreement with the results obtained.*

The 2′/4′ ratios for the nitration of 4-nitro-, 2-nitro-, and 2 : 4-di-nitro-diphenyl are seen from the above figures to be in the proportion 59 : 64 : 82, and if it be assumed that the 2′/4′ ratio is determined, as it is in the case of the monohalogenobenzenes, by the degree of electropositiveness of the substituent (the *o*/*p* ratios for Cl, Br, and I in those compounds are as 43 : 61 : 70, corresponding to increasing positiveness of the halogen atom), then in 4-nitrodiphenyl (I) carbor atom 1 (in nucleus B) should be less positive than the correspondin atom in 2-nitrodiphenyl, this C_1 being in turn less positive than tha in 2 : 4-dinitrodiphenyl. And this is the case, in effect if not in fact owing to the polarising effect of the nitro-group or groups. I seems probable, therefore, that the properties of C_1, as affected b the substituents attached to the other carbon atoms of the B nucleus determine the ratio of 2′ to 4′ nitration (*i.e.*, *o*- to *p*-nitration i nucleus A). It is possible that, if certain strongly polarising group

(I.) 

could be introduced into B, C_1 would become so positive that som 3′-nitration would occur in A.

By nitrating 3-nitrodiphenyl, Blakey and Scarborough (J., 192 3000) obtained 11—12 g. of 3 : 4′- and 5—6 g. of 2 : 3′-dinitr diphenyl out of a total possible 18 g. of dinitro-derivatives, ar although these figures are only approximate, they are in accordan with the expectations of the above theory, which requires a 2′/

ratio even lower than that of 4-nitrodiphenyl, for C_1 in 3-nitrodiphenyl possesses a distinctly negative character.

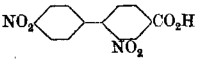
Bell, Kenyon, and Robinson (J., 1926, 1239) showed that diphenyl, when mononitrated by a mixture of nitric and acetic acids at 80—90°, gave 45—55% of 4-nitrodiphenyl. We have dinitrated diphenyl quantitatively, and find that 30% of the product is 4 : 4'-dinitrodiphenyl. Since this must have been derived from intermediately formed 4-nitrodiphenyl, which, as shown above, is nitrated to the extent of 63% in the 4'-position, it can be calculated that, of the original diphenyl, 47% must have been nitrated in position 4, and therefore 53% in position 2, a result not in disagreement with the observations of Bell, Kenyon, and Robinson.

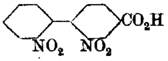
4 : 4'-Dinitrodiphenyl is readily nitrated by hot fuming nitric acid, and the 2 : 4 : *4'-trinitrodiphenyl* formed is nitrated in presence of mixed acids at 100° to give the known 2 : 4 : 2' : 4'-tetranitro-compound. 2 : 2'-Dinitrodiphenyl is similarly nitrated to give mainly 2 : 4 : *2'-trinitrodiphenyl* (convertible in turn into the above tetranitro-compound), together with a small quantity of a second substance.

The mononitration of 2 : 4'-dinitrodiphenyl, which has been studied quantitatively, produces 47·5% of 2 : 4 : 2'- and 52·5% of 2 : 4 : 4'-trinitrodiphenyl, a result which appears to show the very *small effects originating from mere steric influences.*

When picryl chloride, iodobenzene, and copper bronze are heated together, the main product is 2 : 4 : *6-trinitrodiphenyl*, the apparent non-formation of hexanitrodiphenyl being no doubt due to spatial effects.

We have also studied the nitration of diphenyl-4-carboxylic acid, in an attempt to prepare 4'-nitrodiphenyl-4-carboxylic acid, of which the mononitration (occurring, as it possibly would, in both rings) would have been of considerable interest as affording a method of comparing the retarding influence of the nitro- and the carboxyl group on further substitution. We have, however, been unable to obtain the mononitro-acid, although dinitration is readily accomplished, and has been studied quantitatively. Only two dinitro-acids are formed, and these are readily separated by fractional acidification of the alkaline solution of the mixture. One acid (m. p. 265°, corr.), constituting 49% of the total product, is clearly identical with that (m. p. 252°) described by Strasser and Schultz

(II.) 

 (III.)

(*Annalen*, 1881, **210**, 191), who obtained evidence that it was 2 : 4'-dinitrodiphenyl-4-carboxylic acid (II). That the conclusion

of these authors is correct has now been shown by decarboxylating the acid, whereby 2 : 4′-dinitrodiphenyl was isolated.

The second acid, forming 51% of the product, is *2 : 2′-dinitrodiphenyl-4-carboxylic acid* (III), since decarboxylation affords 2 : 2′-dinitrodiphenyl. Strasser and Schultz suspected the presence of a second acid, but failed to isolate it.

Although the nitration of 4′-nitrodiphenyl-4-carboxylic acid could not be studied, the results obtained clearly show that the retarding influence of a nitro-group is far greater than that of a carboxyl group.

EXPERIMENTAL.

(All melting points given are corrected.)

Nitration of 4-Nitrodiphenyl.—4-Nitrodiphenyl (20 g.) was added to 285 c.c. of nitric acid (*d* 1·448), stirred, and kept at 40—50°. 4 : 4′-Dinitrodiphenyl gradually separated, and stirring was continued until the temperature of the suspension had fallen to 20°. The solid was then filtered off and washed with dilute nitric acid, 13·65 g. of 4 : 4′-dinitrodiphenyl, m. p. 239—243°, being obtained. The mother-liquor was precipitated with water, and yielded 10·75 g. of crude 2 : 4′-dinitrodiphenyl, so the total yield of dinitrodiphenyls was 99·5% of that theoretically possible. The amount of 4 : 4′-dinitrodiphenyl not separating under the above conditions was determined as follows: A "mother-liquor" having the same composition as that in the actual nitration was prepared by stirring a mixture of 71·5 c.c. of nitric acid (*d* 1·448), 0·5 c.c. of water, 2·7 g. of 2 : 4′-dinitrodiphenyl and 3·4 g. of 4 : 4′-dinitrodiphenyl, the temperature being allowed to fall slowly from 50° to 20°. The undissolved 4 : 4′-dinitrodiphenyl weighed 3·0 g. The corrected weight of 4 : 4′-isomeride is therefore 13·65 + 1·6 = 15·25 g., whence the percentage in the total nitration product is 62·5.

In a second nitration, 10 g. of 4-nitrodiphenyl gave 4·98 g. of crude 2 : 4′-isomeride, and 7·02 + 0·69 = 7·71 g. of 4 : 4′-compound, corresponding to 64% of 4 : 4′-nitration.

The crude 2 : 4′-compound was crystallised several times from alcohol. Although the amount of 4 : 4′-compound present was small, as the solubility control experiment showed, it was difficult to remove it, owing to the solubility of 4 : 4′-dinitrodiphenyl in concentrated alcoholic solutions of 2 : 4′-dinitrodiphenyl and its sparing solubility in dilute alcoholic solutions of its isomeride.

Dinitration of Diphenyl.—Diphenyl (20 g.) was added gradually to 440 c.c. of nitric acid (*d* 1·448), kept stirred and initially at 35° The temperature rose to 50°, and was kept at that point by external cooling. After all the hydrocarbon had been added, the solution was stirred until it had cooled to 20°. 4 : 4′-Dinitrodipheny

crystallised out, and was filtered off; its weight, after correction for solubility in the mother-liquor (determined with the appropriate solution), was 9·43 g. Complete precipitation of the original mother-liquor gave 23·77 g. of solid. The total yield of isomeric dinitro-compounds was thus 97% of that theoretically possible. Since the 4 : 4′-dinitrodiphenyl (29·8% of total product) must have been formed from 4-nitrodiphenyl, which undergoes 63% of 4′-nitration, the original diphenyl must have undergone

$$\frac{9{\cdot}43 \times 199 \times 154 \times 100}{244 \times 0{\cdot}63 \times 20 \times 199} = 47\% \text{ of 4-nitration.}$$

In a second experiment, 9·83 g. of diphenyl gave a corrected weight of 4·61 g. of 4 : 4′-dinitrodiphenyl (total yield of dinitro-compounds, 15·53 g. = 98%). From this result, the original diphenyl must have undergone 47% of 4-nitration (4 : 4′-compound, 29·7% of total product).

Nitration of 4 : 4′-Dinitrodiphenyl.—The dinitro-compound was dissolved in 10 parts of nitric acid (*d* 1·5) and the solution was heated to boiling for a few minutes, cooled, and poured into water. The precipitated solid, when washed and dried, had m. p. 175—176°, and crystallised from glacial acetic acid or from nitric acid in pale yellow cubes, m. p. 176° (Found: N, 14·9. $C_{12}H_7O_6N_3$ requires N, 14·6%).

The 2 : 4 : 4′-*trinitrodiphenyl* so obtained was nitrated as follows: 1 G. was dissolved in 10 c.c. of concentrated sulphuric acid, 10 c.c. of nitric acid (*d* 1·5) were added, and the mixture was heated at 100° for an hour; the cooled solution was poured into water. The precipitated solid crystallised from glacial acetic acid in small needles, m. p. 165°, and was identical with 2 : 4 : 2′ : 4′-tetranitrodiphenyl obtained by the Ullmann synthesis.

Preparation of 2-Nitrodiphenyl.—Diphenyl was nitrated by the method of Bell and Kenyon (J., 1926, 1239). The acetic acid mother-liquors, obtained after removal of solid 4-nitrodiphenyl, were poured into water. The oil was separated, washed with warm water, dried, and slowly distilled at 20 mm. through a short column. The fraction of b. p. 185—190° was almost pure 2-nitrodiphenyl. It was dissolved in methylated spirit so as to give a solution saturated at 20°. This was cooled to 0° and inoculated with 2-nitrodiphenyl. The material which crystallised was submitted to a similar process, whereupon pure 2-nitrodiphenyl was obtained, m. p. 37—38°.

Nitration of 2-Nitrodiphenyl.—(a) *Qualitative.* 2-Nitrodiphenyl (20 g.) was stirred with 270 c.c. of nitric acid (*d* 1·420) at 35°, and nitric acid (*d* 1·5) was added very slowly. The temperature rose slightly, and the 2-nitrodiphenyl first melted and then slowly

dissolved. After all had passed into solution, the liquid was stirred for a further ½ hour, water added gradually until the temperature rose to 50°, and the liquid allowed to cool. 2 : 4′-Dinitrodiphenyl separated and, after being twice crystallised from alcohol, had m. p. 92·5—93·5° (10 g.). The mother-liquor was completely precipitated with water, and the solid precipitate was crystallised repeatedly from benzene and then from alcohol, pure 2 : 2′-dinitrodiphenyl being obtained.

(b) *Quantitative.* 2-Nitrodiphenyl (4 g.) was nitrated under the foregoing conditions. After the addition of water, resulting in a rise of temperature to 50°, the whole was poured into excess of cold water and left over-night. The solid deposit was filtered off, well washed with boiling water, partly dried, powdered, and then dried in a vacuum over calcium chloride. In this way, 4·79 g. (yield, 97·7%) and 4·83 g. (yield, 98·5%) of mixed dinitrodiphenyls were obtained in two different experiments. Both specimens had f. p. 68·3°. The f. p.'s of a number of mixtures of 2 : 2′- and 2 : 4′-dinitrodiphenyl were then accurately determined:

2 : 4′-Compound, %	0·0	21·5	47·5	59·9	60·8	69·6	78·2	88·7	100·0
F. p.	123·6°	109·2°	85·6°	70·4°	69·1°	74·2°	79·2°	85·4°	91·3°

The f. p. of the nitration product is thus 0·5° lower than the eutectic point (39% of 2 : 2′-compound). Addition of 0·6218 g. of 2 : 4′-compound to 1·3643 g. of nitration product gave a mixture of f. p. 75·6°, corresponding with 28·2% of 2 : 2′-dinitrodiphenyl, or with 27·4% of that compound if it be assumed that the nitration product has the same composition as the eutectic. It follows from this that 2-nitrodiphenyl undergoes about 61% of 4′-nitration, and therefore about 39% of 2′-nitration, the amount of nitration in any other sense being of the order of 1%.

Preparation of 2 : 4-Dinitrodiphenyl.—A mixture (equimolecular) of 21 g. of iodobenzene and 20 g. of 1-chloro-2 : 4-dinitrobenzene was heated in a wide-mouthed conical flask in a metal-bath, initially at 210°. Copper bronze (40 g.) was added gradually, the mixture being well stirred with a thermometer. The temperature of the mixture rose slowly to 225°, and reaction proceeded rapidly. After all the copper had been added, heating was continued (230°) for 10 minutes. The cooled product was extracted with hot benzene, and the extract distilled in steam. No diphenyl was detected. The non-volatile oil was crystallised from 200 c.c. of hot methylated spirit. 2 : 4-Dinitrodiphenyl was then obtained (3—5 g.) in golden-yellow plates, m. p. 110° (Found: N, 11·6. $C_{12}H_8O_4N_2$ requires N, 11·5%). further quantity remained in the mother-liquors.

Nitration of 2 : 4-Dinitrodiphenyl.—2 : 4-Dinitrodiphenyl (2

was dissolved in 50 c.c. of nitric acid (*d* 1·5). The solution was heated at 100° for a minute, cooled, and poured into water. The precipitated solid was filtered off, washed with warm water, and dried in a vacuum over calcium chloride. In this way, 2·35 g. (yield, 99%) of mixed trinitro-derivatives were obtained, f. p. 139·5°. The f. p.'s of a number of mixtures of 2 : 4 : 4'- and 2 : 4 : 2'-trinitrodiphenyl (see below) were then determined :

2 : 4 : 4'-Compound, %	0·0	50·6	53·9	55·6	65·1	80·7	90·1	100·0
F. p.	150·5°	134·6°	138·0°	140·8°	148·7°	162·4°	169·2°	175·5°

A mixture of 1·0028 g. of nitration product with 0·9614 g. of pure 2 : 4 : 4'-trinitrodiphenyl had f. p. 159°, corresponding to 23·5% of 2 : 4 : 2'-trinitrodiphenyl. The calculated percentage of 2 : 4 : 2'-derivative in this new mixture is 23·0%, the absence of any third substance being assumed. It follows that the nitration product contained 55% of 2 : 4 : 4'- and 45% of 2 : 4 : 2'-trinitrodiphenyl.

Nitration of 2 : 2'-*Dinitrodiphenyl.*—The dinitro-compound (6 g., m. p. 124°) was added gradually to 60 c.c. of nitric acid (*d* 1·5), which was kept at 75—80°; water was then slowly added, the temperature being kept below 80°, until crystallisation began, whereupon the whole was allowed to cool. The solid was filtered off, washed with water, and twice crystallised from glacial acetic acid, 5·4 g. of pure 2 : 4 : 2'-*trinitrodiphenyl* being obtained as pale yellow rectangular prisms, m. p. 150—151° (Found: N, 14·8. $C_{12}H_7O_6N_3$ requires N, 14·6%).

The nitration mother-liquor, when treated with excess of water, gave 1 g. of a mixture of trinitro-compounds, and the acetic acid mother-liquor yielded 0·5 g. of gummy material. The results show that 2 : 2'-dinitrodiphenyl is nitrated to the extent of 80—85% in position 4.

Nitration of 2 : 4 : 2'-*Trinitrodiphenyl.*—The foregoing compound (1 g.) was heated with 10 c.c. of concentrated sulphuric acid and 10 c.c. of nitric acid (*d* 1·5) at 100° for 1 hour, the solution cooled, and poured into water. The precipitated solid, after being twice crystallised from glacial acetic acid, melted at 165°, and was identical with a specimen of 2 : 4 : 2' : 4'-tetranitrodiphenyl prepared by the Ullmann process from 1-chloro-2 : 4-dinitrobenzene.

Nitration of 2 : 4'-*Dinitrodiphenyl.*—A solution of 5 g. of the dinitro-compound (m. p. 93·5°) in 30 c.c. of nitric acid (*d* 1·5) was heated at 100° for one minute and poured into water; the precipitated solid was carefully washed and dried, and then had f. p. 136·9°. The addition of a weighed quantity of pure 2 : 4 : 4'-trinitrodiphenyl raised the f. p. by the amount corresponding to the absence of a third substance. Hence, from the data given above,

2 : 4′-dinitrodiphenyl undergoes 52·5% of 4-nitration and 47·5% of 2′-nitration.

2 : 4 : 6-*Trinitrodiphenyl.*—A mixture of 30 g. of picryl chloride and 30 g. of iodobenzene was heated in a bath at 195—200°. The mixture was stirred with a thermometer, and 25 g. of copper bronze were gradually added, the temperature not being allowed to rise above 205°. The cooled mixture was extracted with hot alcohol. The crystalline solid separating on cooling was recrystallised from light petroleum (b. p. 80—100°; Soxhlet extractor) and then from alcohol. 2 : 4 : 6-*Trinitrodiphenyl* forms pale yellowish needles, m. p. 130° (Found: N, 15·2. $C_{12}H_7O_6N_3$ requires N, 14·6%). No hexanitrodiphenyl was detected.

Preparation of Diphenyl-4-carboxylic Acid.—(a) *From 4-amino-diphenyl.* This compound gives very poor yields of 4-cyanodiphenyl by the diazo-method (compare Kaiser, *Annalen*, 1890, **257**, 95; Ferriss and Turner, J., 1920, **117**, 1140).

(b) *From 4-acetyldiphenyl.* This compound was prepared by a modification of the method given previously (Ferriss and Turner, *loc. cit.*): To a mixture of 125 g. of diphenyl, 40 g. of acetyl chloride, and 500 c.c. of carbon disulphide, 90 g. of well-powdered aluminium chloride were slowly added (10 mins.; efficient cooling). The whole was heated on the water-bath for 2 hours and then cooled and decomposed with water. Carbon disulphide and excess of diphenyl were removed in a current of steam, and the residual oil was distilled in superheated steam from a flask kept in a bath at 200°. The crude 4-acetyldiphenyl so obtained was suitable for the next preparation; after crystallisation from alcohol it had m. p. 120·5° (60—70 g.). It was oxidised by one of the following methods.

Hypochlorite oxidation. A mixture of 5 g. of acetyldiphenyl with 150 c.c. of water was boiled and 30 c.c. of commercial sodium hypochlorite solution were added gradually. Boiling was continued until chloroform was no longer evolved, the hot liquid was then filtered and acidified, and the precipitated solid crystallised twice from alcohol to remove terephthalic acid; 2 g. of diphenyl-4-carboxylic acid were thus obtained.

Permanganate oxidation. To a vigorously stirred, boiling suspension of 50 g. of finely powdered acetyldiphenyl in 1 l. of water were added 120 g. of potassium permanganate in six portions at ½-hour intervals. The mixture was finally boiled for a further hour, filtered whilst hot, and then decolorised with sulphur dioxide. On addition of hydrochloric acid, crude diphenylcarboxylic acid was precipitated. After removal of terephthalic acid by two crystallisations from alcohol, 40 g. of acid, m. p. 228°, were obtained. If all

the permanganate is added at the beginning, more terephthalic acid is produced.

Experiments on the Nitration of Diphenyl-4-carboxylic Acid.—(a) *In concentrated sulphuric acid.* Nitration with mixed acids is impossible, owing to the readiness with which the carboxylic acid undergoes sulphonation. The ready sulphonation of diphenyl compounds has been noted frequently in this series of investigations, but has not been reported previously.

(b) *In glacial acetic acid.* Trial experiments showed that nitration did not occur, or was incomplete, unless about 4 mols. of nitric acid were present. Mononitration could not be effected. For dinitration, the most satisfactory conditions were as follows: 2 G. of diphenylcarboxylic acid were dissolved in 15 c.c. of boiling glacial acetic acid, and 1·4 c.c. (4 mols.) of nitric acid (*d* 1·5) were added. After the mixture had been kept at the b. p. for a short time, dinitration was complete, the product having m. p. 180—245°.

(c) *In nitric acid.* Diphenylcarboxylic acid does not dissolve in nitric acid of *d* 1·4, but dissolves in the acid of *d* 1·5 at 0°, to give the result recorded by Strasser and Schultz (*loc. cit.*). Their dinitro-acid was isolated with m. p. 254° (265° corr.). The very sparingly soluble compound described by them is apparently a polynitro-compound.

Diphenylcarboxylic acid dissolved slowly in well-stirred nitric acid (*d* 1·5) at −15° to give only dinitro-acids. The solution was poured into water, and the precipitated solid collected, washed, and dried (Found: N, 9·9. $C_{13}H_8O_6N_2$ requires N, 9·7%).

Quantitative Dinitration of Diphenyl-4-carboxylic Acid.—The acid (16·24 g.) was added to 610 c.c. of well-stirred nitric acid (*d* 1·5) kept at −15°, stirring being maintained until a clear solution was obtained. This was poured on ice, and the solid obtained was filtered off, washed, and dried in a vacuum over calcium chloride (20·2 g.). The mother-liquor was almost neutralised with sodium carbonate. The gum which separated became crystalline when the whole was heated at 100°. The solid, after being collected and purified as before (3·34 g.), had m. p. 194—195°. The total yield (23·54 g.) is almost theoretical.

The fraction weighing 20·2 g. was suspended in 400 c.c. of hot water, and just sufficient sodium carbonate added to give a clear solution, which was diluted to 4 l. and stirred vigorously. Hydrochloric acid (about 0·75*N*) was added drop by drop, and from time to time precipitates were filtered off. In this way, a sharp separation into two main fractions was effected: (1) m. p. 240—254°, 11·60 g., crystallising from alcohol-acetic acid in small colourless needles, m. p. 265° (corr.); (2) m. p. 191—197°, 8·55 g. The above substance

of m. p. 194—195° was the same, so that the total yield of (2) was 11·89 g., whence the percentages of (1) and (2) are respectively 49 and 51.

The constitutions of the two acids were determined by decarboxylation. After several methods had been tried, the following proved successful: 1·5 G. of acid (1) were well ground with 2 g. of sodium hydrogen carbonate and 3·5 g. of copper bronze, and the mixture was slowly heated in a bath. At 305°, the metallic appearance of the copper suddenly vanished, and the mixture became pasty. It was cooled, and extracted twice with boiling benzene. Four similar experiments were carried out, and the combined extracts were evaporated. *The oily residue became crystalline on cooling. After* being crystallised first from light petroleum (b. p. 80—100°) and then from alcohol, it (0·4 g.) had m. p. 92·5—93·5°, unaffected by admixture of pure 2 : 4′-dinitrodiphenyl. *Acid (1) is therefore* 2 : 4′-dinitrodiphenyl-4-carboxylic acid.

Acid (2), similarly treated, gave a crude product melting at *110—118°. After successive crystallisation from light petroleum* (b. p. 80—100°) and alcohol, it melted at 124°, either alone or when mixed with pure 2 : 2′-dinitrodiphenyl. Acid (2) is therefore 2 : 2′-dinitrodiphenyl-4-carboxylic acid.

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EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, December* 31*st*, 1928.]

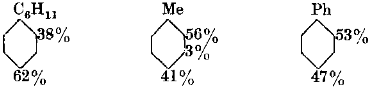
LXXIV.—*The Nitration of Phenyl*cyclo*hexane and of its* p-*Halogeno-derivatives.*

By HORACE ALFRED MAYES and EUSTACE EBENEZER TURNER.

ALTHOUGH Kursanoff (*Annalen*, 1901, **318**, 309) nitrated phenylcyclohexane, he isolated only one product, which he showed to be *p*-nitrophenyl*cyclo*hexane. In view of the important relationship the hydrocarbon bears to diphenyl on the one hand and to toluene homologues on the other, we have studied its nitration quantitatively, and compared the ortho-directing influence of the *cyclo*hexyl group with those of chlorine and bromine by studying the nitration of the *p*-halogenophenyl*cyclo*hexanes.

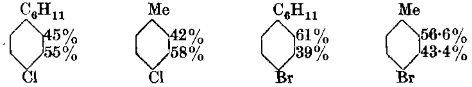
Phenyl*cyclo*hexane is nitrated to give 62% of *p*-nitro- and 38% of *o*-nitro-compound, with possibly a trace of a third substance, and it is of value to compare its nitration with those of toluene (Holleman, *Proc. K. Akad. Wetensch, Amsterdam*, 1908, **11**, 248; *Re*

trav. chim., 1909, **28**, 408) and diphenyl (Gull and Turner, preceding paper):



From these figures it is seen that the three *o/p* ratios are 0·61, 1·37, and 1·13 respectively. It is by no means clear why phenyl*cyclo*hexane should give so low an *o/p* ratio, although, of course, the *cyclo*hexyl radical (like the *tert.*-butyl) may exert a considerable steric effect in opposition to *o*-substitution. This is in interesting contrast to the small steric effect of the phenyl and *o*-nitrophenyl radicals (Gull and Turner, *loc. cit.*).

Numerous experiments were necessary before the conditions for mononitration of p-*chloro*- and p-*bromo-phenyl*cyclo*hexane* could be discovered, but the results ultimately obtained afford an instructive comparison with those recorded by Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 257; *Rec. trav. chim.*, 1915, **34**, 283) for the nitration of *p*-chloro- and *p*-bromo-toluene:



Nitration of *p*-chlorophenyl*cyclo*hexane occurs more in position 2 than in the case of *p*-chlorotoluene, in spite of the relative *o/p* ratios for the *cyclo*hexyl and methyl groups. At the moment there is no theory capable of explaining such results. p-*Iodophenyl*cyclo*hexane* cannot be caused to undergo simple nitration, the main product of the action of nitric acid being *p*-iodonitrobenzene. Willgerodt and Hilgenberg (*Ber.*, 1909, **42**, 3832) obtained *p*-di-iodobenzene by treating diphenyl with iodine and nitric acid in light petroleum, and Professor Robinson has directed our attention to a paper by Mrs. Robinson (J., 1916, **109**, 1078) in which similar results were recorded with derivatives of anisole.

Nitration of phenyl*cyclo*hexane may also lead to 2 : 4-dinitrophenyl*cyclo*hexane, readily oxidisable to 2 : 4-dinitrobenzoic acid and reducible to 2 : 4-*diaminophenyl*cyclo*hexane*. The latter is also obtained by reducing 2-*nitro*-4-*aminophenyl*cyclo*hexane*, which is the product of nitrating *p*-aminophenyl*cyclo*hexane in presence of excess of sulphuric acid. These interconversions establish the constitutions of the substances involved.

Dinitration of *p*-chlorophenyl*cyclo*hexane gives a chlorodinitro-compound which is identical with the product obtained by nitrating *4-chloro-2-nitrophenyl*cyclo*hexane*. The dinitro-compound reacts with piperidine, and must therefore be either the 2 : 3- or the 2 : 5-derivative. Since in this reaction a chlorine atom and not a nitro-group is replaced, the dinitro-compound is probably *4-chloro-2 : 5-dinitrophenyl*cyclo*hexane* (see note below).

It was originally hoped to study the nitration of a number of compounds allied to phenyl*cyclo*hexane. Phenyl*cyclo*hexene could not be caused to undergo simple nitration under a very large variety of experimental conditions. Phenyl*cyclo*hexane readily condenses with acetyl chloride in presence of aluminium chloride to give p-*acetylphenyl*cyclo*hexane* (4-cyclo*hexylphenyl methyl ketone*), from which 4-cyclo*hexylbenzoic acid* is readily obtainable by oxidation. The constitution of the acid was established by its synthesis from the nitrile obtained normally from *p*-aminophenyl*cyclo*hexane.

EXPERIMENTAL.

*Phenyl*cyclo*hexane*.—This substance was obtained by Kursanoff's method (*loc. cit.*), excepting that the reaction between *cyclo*hexyl chloride, benzene, and aluminium chloride was completed by a short heating at 100°. The yield of the pure hydrocarbon, b. p. 115°/15 mm. or 132°/30 mm., was 76% (Kursanoff, 50%). The required *cyclo*hexyl chloride was prepared by dissolving *cyclo*hexanol in about 1½ times its volume of concentrated hydrochloric acid, saturating the solution with hydrogen chloride, and heating it under reflux for 2 hours. A little *cyclo*hexene is the only by-product, and the yield is 60—70%.

p-*Chlorophenyl*cyclo*hexane*.—*cyclo*Hexyl chloride (62 g.) was slowly added to a well-shaken mixture of chlorobenzene (160 g.) and aluminium chloride (14 g.), which was not cooled. The yield of p-*chlorophenyl*cyclo*hexane*, a colourless liquid, b. p. 145°/19 mm., 140°/15 mm., and 134°/10 mm., $d_{4^{\circ}}^{20^{\circ}}$ 1·065, $n_D^{20^{\circ}}$ 1·5386, was 74 g. (Found: Cl, 18·3. $C_{12}H_{15}Cl$ requires Cl, 18·3%). The constitution of the chloro-compound was shown by oxidation: The compound (2 g.) was stirred with a solution of 20 g. of sodium dichromate in 60 c.c. of water, and 45 c.c. of concentrated sulphuric acid were then added slowly; the temperature rose until oxidation set in, and at this point acid was added at such a rate that the oxidation proceeded smoothly (unless care is exercised, the reaction becomes violent). After addition of the acid, the mixture was stirred for ½ hour, heated to 100°, and diluted. The precipitated *p*-chlorobenzoic acid was filtered off and crystallised from alcohol. It had m. p. 236°, alone or mixed with an authentic specimen of the ac

The chloro-compound was also obtained in poor yield from the corresponding amino-compound by the Sandmeyer reaction.

p-*Bromophenyl*cyclo*hexane*.—Using a method similar to that for the chloro-compound, we obtained the *bromo*-compound as a colourless liquid, b. p. 160°/23 mm., $d_4^{25°}$ 1·283, $n_D^{25°}$ 1·5584, in 65% yield (Found : Br, 33·0. $C_{12}H_{15}Br$ requires Br, 33·5%). Oxidation by the dichromate method gave a product containing chromium compounds which could only be removed with considerable difficulty; *p*-bromobenzoic acid was, however, obtained. The bromo-compound was also prepared, although in poor yield, by the Sandmeyer reaction from *p*-aminophenyl*cyclo*hexane; it had $n_D^{25°}$ 1·5579.

p-*Iodophenyl*cyclo*hexane*.—This *substance* was obtained in good yield by adding diazotised *p*-aminophenyl*cyclo*hexane to potassium iodide solution; it is an oil, b. p. 185°/21 mm. or 174°/11 mm., $d_4^{19°}$ 1·448, $n_D^{25°}$ 1·5900 (Found : I, 44·2. $C_{12}H_{15}I$ requires I, 44·4%).

*Nitration of Phenyl*cyclo*hexane*.—Kursanoff (*loc. cit.*) cooled the hydrocarbon in ice and added excess of fuming nitric acid. This procedure is inadvisable, since with too efficient cooling the hydrocarbon solidifies, whereas with inefficient cooling a violent reaction ·ay set in. The following methods were found suitable :

(1) Phenyl*cyclo*hexane (58 c.c.) was slowly added to 210 c.c. of ric acid (*d* 1·5), kept well stirred and cooled to 0°. Stirring was ntinued for a short time after the addition was complete, and the ution was then poured on ice, and the semi-solid product extracted th benzene. The extract, after being washed successively with ter, alkali, and water, was dried over calcium chloride, and most the benzene removed at ordinary pressure. The residue, b. p. 5—225°/25 mm., was separated by repeated distillation into two ctions, A and B.

(2) A saturated solution of phenyl*cyclo*hexane (100 g.) in glacial etic acid (190 c.c.) was slowly added to a mixture of 375 c.c. of ric acid (*d* 1·5) and 160 c.c. of glacial acetic acid, the temperature ing kept at 0°. After addition was complete, the mixture was kept rred for ½-hour, poured on ice, and worked up as before. Fracnal distillation gave two fractions, A and C.

Fraction A, b. p. 198°/16 mm. or 210°/25 mm., solidified on cooling, d after crystallisation from alcohol formed pale yellow plates, p. 58·5°. This was identical with Kursanoff's *p*-nitrophenyllohexane, m. p. 57·5—58·5° (Found : N, 7·0. Calc. : N, 6·8%). ırsanoff oxidised his product with dilute nitric acid (35 hours at 5—140°), but the dichromate method has been found to give nost quantitative yields of *p*-nitrobenzoic acid.

Fraction B, b. p. 222°/15 mm., also solidified on cooling, and parated from alcohol in pale yellow platelets, m. p. 57° (Found :

N, 11·9. $C_{12}H_{14}O_4N_2$ requires N, 11·2%). Oxidation with dichromate gave 2 : 4-dinitrobenzoic acid, so the product was 2 : 4-*dinitrophenyl*cyclo*hexane*.

Fraction C, b. p. 174°/16 mm., $d_{4^\circ}^{25^\circ}$ 1·111, $n_D^{25^\circ}$ 1·5472, remained as an oil (Found : N, 7·1. $C_{12}H_{15}O_2N$ requires N, 6·8%). Oxidation caused complete destruction of the molecule, but the oil was shown to be the expected o-*nitrophenyl*cyclo*hexane* by its conversion into 2 : 4-dinitrophenyl*cyclo*hexane, which was also formed from the *p*-isomeride.

*Quantitative Nitration of Phenyl*cyclo*hexane.*—The nitration was effected in acetic acid solution (method 2, above). Over 95% of the product consisted of the *o*, *p*-mixture. Its composition was determined by three methods.

(1) *Fractional distillation.* Repeated distillation under reduced pressure of 380 g. of the mixture gave 230 g. of pure *p*-compound the proportion of which in the mixture is, therefore, not less than 60%.

(2) *Oxidation.* As stated above, *p*-nitrophenyl*cyclo*hexane is almost quantitatively oxidised to *p*-nitrobenzoic acid, whilst the *o*-isomeride is destroyed. An artificial mixture of 0·740 g. of *o* with 1·440 g. of *p*-nitro-compound was oxidised by the dichromat method, 1·155 g. of *p*-nitrobenzoic acid being obtained (Calc 1·170 g.; 98·7% yield). When 2·145 g. and 2·490 g. of the nitratio product were similarly oxidised in two different experiment 1·089 g. and 1·205 g. of *p*-nitrobenzoic acid were obtained, corre sponding to 62·4 and 59·4% of *p*-nitrophenyl*cyclo*hexane, or, afte correction on the basis of the above 98·7% yield, to 63·2 and 60·2% (mean, 61·7%).

(3) *Thermal analysis.* Preliminary experiments showed that would only be necessary to determine half of the freezing-poi curve for mixtures of *o*- and *p*-nitrophenyl*cyclo*hexane. Th following freezing points were observed, following the procedu described in a previous paper (J., 1928, 691) :

p-Nitro-compound, %	100	77·8	67·7	65·4	60·5
F. p.	56·7°	44·3°	38·3°	35·7°	32·0

Three different nitration products had f. p. (1) 34·5°, (2) 34·5°, a (3) 32·0°, corresponding respectively to (1) 63·0%, (2) 63·0% a (3) 60·5% of para-compound (mean, 62·2%).

p-*Aminophenyl*cyclo*hexane.*—Kursanoff obtained this compou m. p. 54—56°, by reducing the nitro-compound with tin and hyd chloric acid. We have found iron, water, and a little hydrochl acid preferable as a reducing agent, giving a base of m. p. 55° almost theoretical yield. The *acetyl* derivative melts at 1 (Found : N, 6·6. $C_{14}H_{19}ON$ requires N, 6·5%).

Nitration of p-*Aminophenyl*cyclo*hexane*.—The dry sulphate (11·2 g.) of the base was dissolved in 60 c.c. of concentrated sulphuric acid, the solution cooled to 0°, and 3 c.c. of nitric acid (*d* 1·5) slowly added. The mixture was kept for a further ½ hour, poured on ice, and the precipitate filtered off. 2-*Nitro*-4-*aminophenyl*cyclo*hexane*, crystallising from alcohol in yellow leaflets, melts at 66° (Found: N, 12·8. $C_{12}H_{16}O_2N_2$ requires N, 12·7%).

2 : 4-*Diaminophenyl*cyclo*hexane*.—Reduction of the corresponding dinitro-compound by the above method with iron gave this *base*, which crystallised from alcohol in colourless needles, m. p. 108° (Found: N, 14·8. $C_{12}H_{18}N_2$ requires N, 14·7%).

Similar reduction of the above nitroamine gave the same diamine. The two specimens of diamine, acetylated separately, gave the same diacetyl compound, separating from alcohol in platelets, m. p. 268°.

Nitration of p-*Chlorophenyl*cyclo*hexane*.—As stated above, the nitration of this compound proved very tedious, owing to the difficulty of securing quantitative mononitration. The comparative insolubility of the compounds themselves, and of the derived nitro-compound, added to the difficulty.

When *p*-chlorophenyl*cyclo*hexane was slowly added to 8 times its weight of nitric acid (*d* 1·5), kept at 0° to −5°, 4-*chloro*-2 : 5-*dinitrophenyl*cyclo*hexane* was obtained in good yield. It crystallises from alcohol in almost colourless plates, m. p. 92° (Found: N, 10·1; Cl, 12·3; *M*, in camphor, 288. $C_{12}H_{13}O_4N_2Cl$ requires N, 9·9; Cl, 12·5%; *M*, 284·5). When warmed with piperidine for a short time, it gave 2 : 5-*dinitro*-4-*piperidinophenyl*cyclo*hexane*, which crystallised from dilute acetic acid in orange-yellow plates, m. p. 108° (Found: N, 12·8. $C_{17}H_{23}O_4N_3$ requires N, 12·6%).

When a solution of 5·3 g. (5 c.c.) of *p*-chlorophenyl*cyclo*hexane in 5 c.c. of glacial acetic acid was added gradually to a mixture of 20 c.c. of nitric acid (*d* 1·5) and 7 c.c. of glacial acetic acid at 5—10°, almost quantitative mononitration occurred. The resulting solution, after being kept at 10° for a short time, was poured on ice, and the whole then extracted with ether. The extract was washed with water, with alkali, and again with water, dried, and freed from solvent by heating at 100°. The residual oil, A, was analysed (Found: Cl, 14·5. $C_{12}H_{14}O_2NCl$ requires Cl, 14·8%). A portion of it was heated for 2—3 hours at 100° with excess of piperidine, which reacted with the 3-nitro- but not with the 2-nitro-compound. The reaction product was treated with water and extracted with benzene; the extract was shaken three times with 60% sulphuric acid to remove piperidine and the piperidino-derivative, then washed with water, dried, and freed from benzene by evaporation. The 4-*chloro*-2-*nitrophenyl*cyclo*hexane* so obtained was dissolved in excess

of nitric acid (*d* 1·5), the solution kept for several hours, and then rapidly diluted. The semi-solid precipitate, after being crystallised from alcohol, had m. p. 90·5—91·5°, and when mixed with the above 4-chloro-2 : 5-dinitrophenyl*cyclo*hexane had m. p. 90·5—92°. Further, when it was heated with piperidine, it gave the above dinitropiperidino-compound, m. p. 105—106·5°, a mixture with the specimen obtained as above melting at 105—107·8°. *p*-Chlorophenyl*cyclo*hexane was apparently not nitrated by ordinary nitric acid (*d* 1·42), but slowly darkened in colour. By vigorously stirring the chloro-compound (2·1 g.) with 10 c.c. of nitric acid (*d* 1·48) at 0° for 1¼ hours, a product, B, was obtained containing Cl, 14·7% corresponding to almost quantitative mononitration.

In order to determine the relative proportions of 2- and 3-nitro compounds present in A and B, one of two methods was employed A number of samples corresponding to A and B were actually examined, but the results obtained with one sample of each origi are alone given.

Method 1. A weighed sample of the nitration product was heate with excess of piperidine on a water-bath for 2—3 hours. Distille water was then added, the mixture thoroughly extracted wit benzene, and the aqueous solution of piperidine hydrochloric analysed. This method was more tedious than the following.

Method 2. The nitration product was weighed into a small wid necked flask, which was fitted with a cork through which passed soda-lime tube (to prevent formation of piperidine carbonate ar carbamate) and a small funnel. Piperidine was added through tl funnel, which was then stoppered to prevent ingress of air. Tl flask was heated for 2—3 hours as before, allowed to cool, and pu dry benzene was added through the funnel. The precipitat piperidine hydrochloride was collected on a Gooch crucible, wash with benzene, and dried at 100°.

Analysis of A. Method 1. 2·2430 G. and 1·6064 g. of t nitration product gave 0·7605 g. and 0·5382 g. of AgCl, when 3-nitro-compound = 56·6 and 56·0%.

Method 2. 1·0420 G. gave 0·2975 g. of piperidine hydrochlori whence 3-nitro-compound = 56·3%.

Analysis of B. 0·5727, 0·6209, and 0·5405 G. of B gave resp tively 0·1610, 0·1743, and 0·1521 g. of piperidine hydrochlori whence 3-nitro-compound = 55·4, 55·3, and 55·5%.

A large number of check nitrations, in which incomplete mo nitration occurred, gave results which supported the above figu

Nitration of p-*Bromophenyl*cyclo*hexane.*—5 G. of the bro compound were stirred with 20 c.c. of nitric acid (*d* 1·475) for hours at 0°. The product, isolated as in the case of the chlo

compound, contained Br, 28·3% (calc. for mononitro-compound: Br, 28·2%). Reactive bromine was determined as piperidine hydrobromide: 0·4190 g. and 0·5600 g. gave 0·0893 g. and 0·1204 g. of the hydrobromide, whence 3-nitro-compound = 36·5 and 36·8%.

In another experiment, 2·55 g. of the bromo-compound were stirred with 10 c.c. of nitric acid (*d* 1·48) for 1¼ hours at 0°. The product contained 28·7% Br, and 0·4100 g. and 0·5010 g. gave respectively 0·0911 g. and 0·1172 g. of piperidine hydrobromide, whence 3-nitro-compound = 38·0 and 40·0%. The most probable value from these experiments is 38%.

As in the case of the chloro-compound, numerous check experiments were performed.

Nitration of p-*Iodophenyl*cyclo*hexane.*—The iodo-compound (2·9 g.; 2 c.c.) was gradually added to 10 c.c. of nitric acid (*d* 1·48), kept stirred at 0°. The dark liquid obtained was poured on ice, the whole was extracted with ether, and the extract washed with alkali, which became red. Routine procedure then gave the nitration product as a dark orange oil which, when kept, deposited crystals. These crystallised from alcohol in very pale yellow needles, m. p. 172°, and were identified as *p*-iodonitrobenzene (analysis, m. p., mixed m. p., and conversion into *p*-nitrophenylpiperidine).

p-*Acetylphenyl*cyclo*hexane.*—Aluminium chloride (11·3 g.) was gradually added to a mixture of 15·8 g. of phenyl*cyclo*hexane, 5 g. of acetyl chloride, and 63 c.c. of carbon disulphide. When the vigorous reaction had abated, the mixture was heated on the water-bath for ½ hour and then treated with dilute hydrochloric acid. The carbon disulphide layer on evaporation gave a solid which crystallised from alcohol in lustrous white plates, m. p. 68—69° (yield, 60%). The *phenylhydrazone*, yellow plates from alcohol, m. p. 105°, became black when kept (Found: N, 9·9. $C_{20}H_{24}N_2$ requires N, 9·6%).

Neutral potassium permanganate was without marked action on the ketone, but when a suspension of 2 g. of the latter in a solution of 3·2 g. of potassium permanganate and 3 g. of sulphuric acid in 200 c.c. of water was boiled, terephthalic acid was formed.

p-cyclo*Hexylbenzoic Acid.*—A suspension of the ketone in excess of dilute aqueous sodium hypobromite was boiled, further hypobromite being added from time to time until the oil present did not solidify on cooling. The cooled mixture was extracted with benzene to remove bromoform, and then concentrated to a small bulk. *Sodium* p-cyclo*hexylbenzoate* separated in white needles (Found: Na, 10·4. $C_{13}H_{15}O_2Na$ requires Na, 10·2%). The free acid crystallised from alcohol in minute plates, m. p. 199°. It was also obtained as follows: *p*-Aminophenyl*cyclo*hexane was diazotised,

and the solution added to sodium cuprocyanide; the nitrile so formed was partially purified by distillation in steam and then boiled with alcoholic potassium hydroxide. Acidification of the product gave a solid, which, after two crystallisations from alcohol, was identical with the above acid.

Note, added January 24th, 1929.—Although the constitution of the above dinitro-derivative of *p*-chlorophenyl*cyclo*hexane was not seriously in doubt, the following additional evidence in its favour has now been obtained.

The chlorodinitro-compound was reduced with iron filings, water, and a little acetic acid at 100°. When the reaction was over, excess of precipitated calcium carbonate was added, and the whole was extracted with ether. On evaporation of the ethereal solution, an oil resulted which rapidly solidified; after being crystallised from dilute alcohol, it had m. p. 92—93°, and after being further crystallised from light petroleum (b. p. 60—80°) formed almost colourless needles (tending to form rosettes), m. p. 95—96° (Found : Cl, 15·4. $C_{12}H_{17}N_2Cl$ requires Cl, 15·8%). This substance is therefore 4-chloro-2 : 3 (or 5)-diaminophenyl*cyclo*hexane.

A saturated alcoholic solution of an equimolecular mixture of the diamine and phenanthraquinone was boiled under reflux for 4 hours. The solution darkened considerably, but no separation of solid occurred even after cooling, and this points to the absence of an *o*-diamine structure.

The diamine formed a sparingly soluble hydrochloride, the aqueous solution of which was readily diazotised. The diazo-solution coupled with alkaline β-naphthol to give a purple azo-derivative, thus indicating the presence of a *p*-diamine and the absence of an o-diamine.

When the diamine was warmed with either manganese dioxide or potassium dichromate and dilute sulphuric acid, an odour resembling that of a *p*-quinone was developed, affording evidence against an *o*-diamine structure.

The diamine is therefore 4-*chloro*-2 : 5-*diaminophenyl*cyclo*hexane*, and the dinitro-compound has the constitution originally assigned to it.

One of us is indebted to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

EAST LONDON COLLEGE,
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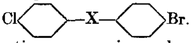
LXXV.—*The Nitration of 4-Chloro-4'-bromo-benzophenone and -diphenylsulphone, and the Attempted Nitration of 4-Chloro-4'-bromodiphenyl.*

By Leslie George Groves and Eustace Ebenezer Turner.

In extension of our studies of nitration of diphenyl derivatives on the one hand (Le Fèvre and Turner, J., 1928, 963, etc.) and of mixed dihalogeno-derivatives on the other (Mayes and Turner, *ibid.*, p. 691), we have investigated the nitration of two compounds of the general formula  In both compounds, X is a meta-orienting group, *viz.*, carbonyl or sulphonyl, and therefore nitration occurs ortho to one halogen or to the other, but not elsewhere. In view of the improbability that the group X will transmit any influences from one nucleus to the other, the results supply information as to the relative rates of nitration in positions ortho to chlorine and to bromine in presence of a constantly acting meta-directing para-substituent.

4-*Chloro-4'-bromobenzophenone* is nitrated to the extent of 51% in position 3 and 49% in position 3'; the values for the nitration of 4-*chloro-4'-bromodiphenylsulphone* are 34 and 66%, respectively. These results are evidently connected with the facts that benzophenone is nitrated readily and diphenylsulphone tardily, and that bromobenzene is nitrated more rapidly than chlorobenzene (Ingold and Shaw, J., 1927, 2918), and has a higher *o/p* ratio than the latter (Holleman, *Rec. trav. chim.*, 1900, **19**, 188, 364; 1905, **24**, 146; 1913, **32**, 134).

We have also attempted to study the quantitative dinitration of 4-*chloro-4'-bromodiphenyl*, but this substance undergoes degradation when submitted to conditions which lead, in the case of 4 : 4'-dichloro- or -dibromo-diphenyl, to almost quantitative 2 : 3'-dinitration.

Experimental.

4-*Chloro-4'-bromobenzophenone*.—Chlorobenzene (32 g.) was slowly added to a gently boiling mixture of 100 g. of carbon disulphide, 50 g. of *p*-bromobenzoyl chloride, and 32 g. of anhydrous aluminium chloride, and boiling was continued for 2 days. Water and a little hydrochloric acid were then added and the mixture was freed from carbon disulphide and chlorobenzene by steam distillation. The residual solid (25 g.) was crystallised several times from alcohol. 4-*Chloro-4'-bromobenzophenone* forms very pale brownish plates,

m. p. 150° (corr.) (Found: AgCl + AgBr, 0·2230 g. $C_{13}H_8OClBr$ requires AgCl + AgBr, 0·2224 g.).

Nitration of 4-Chloro-4'-bromobenzophenone.—To a solution of 3·0 g. of the ketone in 15 c.c. of concentrated sulphuric acid kept at −5°, was slowly added a solution of 1 g. of potassium nitrate in 5 c.c. of concentrated sulphuric acid. When addition was complete, the cooling bath was removed, and the temperature of the nitration mixture rose slowly to 21° before reverting to the temperature of the room. The mixture was poured on ice, and the precipitated solid collected, washed with boiling water, and dried (3·3 g.) (Found: AgCl + AgBr, 0·2236 g. Calc. for $C_{13}H_7O_3NClBr$: AgCl + AgBr, 0·2235 g.).

The mixture of mononitro-derivatives so obtained (0·2472 g.) was heated at 100° for an hour with excess of piperidine. Water was then added, and the precipitated mixture of piperidino-derivatives was filtered off. The filtrate and washings were acidified with dilute nitric acid, and the mixed halogen displaced by piperidine was determined (Found: AgCl + AgBr, 0·1208 g.; atomic ratio of halogen displaced, Cl : Br = 48·8 : 51·2).

A second experiment with the same quantities of material gave AgCl + AgBr, 0·1191; Cl : Br = 53·8 : 46·2. Hence, in mean, 3-nitration = 51·3%, and 3'-nitration = 48·7%.

4-Chloro-4'-bromodiphenylsulphone.—Anhydrous aluminium chloride (1·3 mols.) was slowly added to a mixture of *p*-chlorobenzenesulphonyl chloride (1 mol.) and bromobenzene (2 mols.). The whole was heated on a steam-bath for 2 hours, cooled, poured on ice, and treated with hydrochloric acid. Bromobenzene was removed in a current of steam, and the residual solid thoroughly extracted with alkali to remove unchanged sulphonyl chloride; after being crystallised thrice from alcohol, it formed glistening white needles, m. p. 157° (corr.) (Found: AgCl + AgBr, 0·1896 g. $C_{12}H_8O_2ClBrS$ requires AgCl + AgBr, 0·1888 g.).

Nitration of 4-Chloro-4'-bromodiphenylsulphone.—A solution of 3·315 g. of sulphone in 40 c.c. of concentrated sulphuric acid was slowly treated at the ordinary temperature with a solution of 1·01 g. of potassium nitrate in 20 c.c. of concentrated sulphuric acid (1 c.c. of acid being used for washing). The temperature rose slowly to 22°, and when it had fallen, the solution was poured on ice and the precipitate was filtered off, washed repeatedly with warm water, and dried. It melted under hot water, but solidified on cooling (3·70 g.) (Found: AgCl + AgBr, 0·1550 g.; $BaSO_4$, 0·1101 g. Calc. for $C_{12}H_7O_4NClBrS$: AgCl + AgBr, 0·1559 g.; $BaSO_4$, 0·1098 g.).

The ratio of reactive chlorine to reactive bromine was determined

by the method used above. In one experiment, 0·3001 g. gave 0·1386 g. of AgCl + AgBr; Cl : Br = 31·4 : 68·6. In a second experiment, 0·4215 g. gave 0·1927 g. of AgCl + AgBr; Cl : Br = 35·5 : 64·5. Mean, Cl : Br = 33·5 : 66·5.

Dinitration of 4-Chloro-4′-bromodiphenylsulphone.—Nitric acid (*d* 1·5; 25 c.c.) was added to a solution of 5 g. of the sulphone in 25 c.c. of warm concentrated sulphuric acid. The mixture was heated on the steam-bath for an hour. *4-Chloro-4′-bromo-3 : 3′-dinitrodiphenylsulphone* gradually separated, and in due course the solution was cooled, diluted, and filtered. The m. p., 219° (corr.), was not raised by crystallisation from glacial acetic acid, from which solvent the sulphone separated in pale yellow prisms (Found : AgCl + AgBr, 0·1231 g. $C_{12}H_6O_6N_2ClBrS$ requires AgCl + AgBr, 0·1235 g.). It reacted readily with boiling piperidine to give 3 : 3′-dinitro-4 : 4′-dipiperidinodiphenylsulphone, identical with an authentic specimen of this substance (Le Fèvre and Turner, J., 1927, 1113).

4-Chloro-4′-bromodiphenyl.—4-Chloro-4′-aminodiphenyl (Le Fèvre and Turner, J., 1928, 245) was diazotised in hydrochloric acid solution, and bromine, dissolved in hydrobromic acid, added. The perbromide separated as a bright red crystalline solid, which, after being washed, was suspended in glacial acetic acid. On heating, normal decomposition took place, and the solution on cooling deposited pale brownish needles of *4-chloro-4′-bromodiphenyl*, which, after being crystallised three times from glacial acetic acid, had m. p. 147° (corr.) (Found : AgCl + AgBr, 0·2220, 0·2506 g. $C_{12}H_8ClBr$ requires AgCl + AgBr, 0·2216, 0·2476 g.).

When 2 g. of the chlorobromodiphenyl were added to 30 g. of nitric acid (*d* 1·5) at the ordinary temperature, a deep purple solution was obtained. On gentle warming, the colour faded. The resulting yellowish-brown solution was cooled and slowly diluted with water. About 1·2 g. of a gummy, pale yellow solid were obtained, the composition of which could not be determined. Similar products were obtained when different nitration conditions were employed.

We beg to acknowledge the allocation to one of us of a grant by the Research Fund Committee of the Chemical Society.

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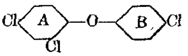
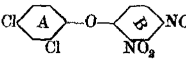
LXXVI.—*The Scission of Diaryl Ethers and Related Compounds by Means of Piperidine. Part II. The Nitration of 2:4:4′-Trichlorodiphenyl Ether, and of 2:4-Dichlorophenyl* p-*Toluenesulphonate and Benzoate.*

By Leslie George Groves, Eustace Ebenezer Turner, and (in part) Gladys Irene Sharp.

If, as Flürscheim contends, residual affinity is a sufficiently descriptive name for the main origin of the factors controlling benzene substitution, then, since the phenoxyl group is very weakly directing (Lea and Robinson, J., 1926, 411), 2 : 4 : 4′-*trichlorodiphenyl ether* (I) might be expected to undergo a certain, although not necessarily a large, amount of nitration in position 3′ in nucleus B. For, according to Flürscheim's view, the effect of the chlorine atoms in positions 2 and 4 will be to release an extra amount of affinity in position 1, so that in effect the oxygen atom is much less unsaturated than it would be in diphenyl ether or in 4 : 4′-dichlorodiphenyl ether, and therefore, on the residual-affinity view, it is even more weakly directing than the oxygen atom in diphenyl ether itself, and approaches, in fact, the directive power of a chlorine atom. On the other hand, on Robinson's view of orientation effects, the conjugation of the oxygen atom will be decreased as a result of the presence of the two chlorine atoms in nucleus A, and further decreased owing to the presence of the 4′-chlorine atom. Its directive power should therefore be increased, and the trichloro-ether would not be expected to undergo nitration at all in position 3′. At the same time, however, the absence of 3′-nitration could not be put forward as necessarily invalidating Flürscheim's theory, owing to the complexity of the case in question.

(I.) 

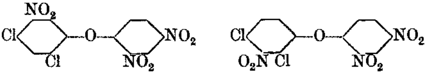
 (II.)

The trichloro-ether was readily obtained from 4 : 4′-*dichloro-2-aminodiphenyl ether* by the Sandmeyer reaction, which has otherwise (see Experimental) given unsatisfactory results in this series, as has also the Gattermann reaction. The amino-ether was obtained from 4 : 4′-dichloro-2-nitrodiphenyl ether.

2 : 4 : 4′-Trichlorodiphenyl ether was *di*nitrated with unexpectedly great readiness, but when, by control of the conditions, mononitration was effected, it took place quantitatively in the 2′-position, the constitution of the product following from its ready scission by mean

of piperidine into 2 : 4-dichlorophenol and 4-chloro-2-nitrophenylpiperidine (compare Le Fèvre, Saunders, and Turner, J., 1927, 1168).

The dinitro-derivative, which was not accompanied by any isomerides, reacted with piperidine to give a mixture of products, amongst which 4-chloro-2-nitrophenylpiperidine and piperidine hydrochloride were recognised (see below), so the second nitro-group must have entered position 3 or 5 in nucleus A. This behaviour was sufficiently unexpected to merit further investigation, and we accordingly studied first the nitration of the more readily accessible 2 : 4-dichloro-2′ : 4′-dinitrodiphenyl ether (II); this was readily mononitrated to give a dichlorotrinitro-ether, unaccompanied by isomerides, which was converted by boiling piperidine into 2 : 4-dinitrophenylpiperidine and a dichloronitrophenol, or by boiling aniline into the latter and 2 : 4-dinitrodiphenylamine. The phenol, although not identical with the known 2 : 4-dichloro-6-nitrophenol, and therefore containing a chlorine atom and a nitro-group ortho to each other, did not react with piperidine. The trinitro-ether was evidently (III) or (IV), and although (III) appeared the more probable, the complete absence of chlorine reactivity on

(III.)  (IV.)

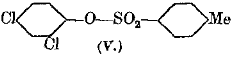
the part of the ether itself made it essential to prove the non-validity of (IV), in which the activating effect of the nitro-group would possibly be masked owing to steric influences. The proof, however, presented unexpected difficulties.

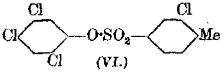
For example, it was anticipated that 2 : 4-dichloro-5-nitroaniline would be convertible by the diazo-method into 2 : 4-dichloro-5-nitrophenol, but we have been unable to effect this change. The base, previously obtained in small yield by Körner and Contardi (*Atti R. Accad. Lincei*, 1909, **18**, 93), is readily obtainable by hydrolysing its *phthalyl* derivative, which is formed in almost quantitative yield by nitrating N-2 : 4-*dichlorophenylphthalimide* (compare Brady, Quick, and Welling, J., 1925, **127**, 2264).

Again, it did not appear improbable that dichlorination of *m*-nitrophenol would give, as one product, 2 : 4-dichloro-5-nitrophenol. Actually, the main, if not the only, product was 2 : 4-*dichloro*-3-*nitrophenol*, identified as follows: its p-*toluenesulphonyl* derivative is reducible to an amino-compound, and replacement of the amino-group by a chlorine atom, followed by hydrolysis of the *p*-toluenesulphonyl group, gives 2 : 3 : 4-*trichlorophenol*. Holleman (*Rec. trav. chim.*, 1920, **39**, 740) obtained the benzoate (m. p. 141°) of this phenol, but not the substance itself. We have now found that

2 : 3 : 4-trichlorophenol is the chief product when 3 : 4-dichlorophenol is monochlorinated, a result of considerable interest. Again, the above result of chlorination of *m*-nitrophenol is somewhat unexpected in view of the fact that *m*-nitroaniline is dichlorinated in the 2 : 6- and the 2 : 4-positions (Körner and Contardi, *loc. cit.*). The constitution of the 2 : 3 : 4-trichlorophenol now described follows by exclusion (apart from the evidence of the m. p. of our benzoate, *viz.*, 143°), since the method used to produce it could only give *2 : 3 : 4-, 2 : 3 : 6-, or 2 : 4 : 5-trichlorophenol. Of these, the last* was in our possession (see below) and the benzoate of the 2 : 3 : 6-compound melts at 90° (Holleman, *loc. cit.*).

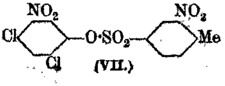
The constitution of the above dichloronitrophenol had therefore to be proved by a less direct method. It was anticipated that since (II) was nitrated *in the meta-position (nucleus A), 2 : 4-dichlorophenyl* p-*toluenesulphonate* (V) would behave similarly. This was


(V.)


(VI.)

found to be the case, for nitration of (V) gave a dinitro-compound, which was converted by boiling piperidine into the above dichloronitrophenol and 1-o-*nitro*-p-*toluenesulphonylpiperidine*, the constitution of which was proved by synthesis. Reduction of the dichlorodinitro-compound gave a diamino-compound which was converted in turn into a tetrachloro-compound. The latter, when boiled *with piperidine, gave a trichlorophenol, the properties* of which agreed with those recorded by Holleman for the 2 : 4 : 5-compound. In view of the method by which Holleman obtained this phenol (*loc. cit.*), it was thought desirable to seek independent evidence as to its properties. This has been done as follows 2 : 5-dichlorophenol, which on monochlorination would be expected to give either 2 : 4 : 5- or 2 : 3 : 6-trichlorophenol, gives the same trichlorophenol as that just mentioned. Additional proof of the constitution was obtained by establishing the identity of the latter with the phenol resulting by the diazo-method from 2 : 4 : 5-trichloroaniline.

It follows from this that the tetrachloro-sulphonate was (VI and that the dinitro-compound from which it was obtained was (VII), so that the dichloronitrophenol is 2 : 4-*dichloro-5-nitrophenol* and the dichlorotrinitrodiphenyl ether is (III) and not (IV).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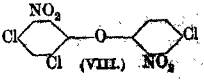

(VIII.)

It would therefore appear probable that the dinitro-derivative of (I) is (VIII). This substance was readily reduced to the corresponding diamino-compound, but attempts to replace the amino-groups by chlorine atoms led to inseparable mixtures. Endeavours to synthesise the expected pentachloro-ether (for seeding purposes) were similarly unsuccessful. 4 : 5-Dichloro-1 : 2-dinitrobenzene was readily converted by potassium *p*-chlorophenoxide into 4 : 5 : 4'-*trichloro-2-nitrodiphenyl ether*, nitration of which gave 4 : 5 : 4'-*trichloro-2 : 2'-dinitrodiphenyl ether*, reducible to a diamino-compound, but the latter could not be converted into the desired pentachloro-ether. Similarly, interaction of the above dichlorodinitrobenzene with potassium 2 : 4-dichlorophenoxide produced 4 : 5 : 2' : 4'-*tetrachloro-2-nitrodiphenyl ether*, also reducible to an amine, but the latter, again, did not react normally under the conditions of a Sandmeyer or Gattermann replacement.

The formation of piperidine hydrochloride when the dinitro-derivative of (I) was heated with piperidine, and the non-formation of this hydrochloride when (III) was so treated, could be explained by assuming that activation of the 4-chlorine atom (formula VIII) by the 5-nitro-group was of an order similar to the activation of the oxygen–$C_{1'}$ linkage by the 2'-nitro-group, so that some scission and some replacement of chlorine by piperidine resulted. Introduction of a third nitro-group into (VIII) in position 6' should make scission much more rapid than replacement of chlorine. The dinitro-compound can be nitrated to give a trichlorotrinitrodiphenyl ether, which is very readily converted into 2 : 4-dichloro-5-nitrophenol, together with a chlorodinitrophenylpiperidine. The readiness of formation of the latter substance suggested that it is 4-*chloro-2 : 6-dinitrophenylpiperidine*, but this compound, prepared for the purpose by treating 4-chloro-2 : 6-dinitroanisole with piperidine, had entirely different properties, so that its isomeride must be either 4-chloro-2 : 5- or 4-chloro-2 : 3-dinitrophenylpiperidine. It seems extremely unlikely that the original nitration could have occurred in the position, *viz.*, 3' in (VIII), corresponding to the production of 4-chloro-2 : 3-dinitrophenylpiperidine, and also that the trichlorotrinitro-ether would have undergone scission prior to replacement of a nitro-group by piperidine. It therefore appears certain that the ether in question is 2 : 4 : 4'-*trichloro-5 : 2' : 5'-trinitrodiphenyl ether*, but in any case the formation of 2 : 4-dichloro-5-nitrophenol in the scission of the trinitro-ether shows that the dinitro-ether is (VIII). Further investigation of the action of piperidine on the latter showed that 76% of this substance undergoes replacement of chlorine by piperidine (it being assumed that only the 4-chlorine atom reacts), and

2 : 4-dichloro-5-nitrophenol was actually isolated from the scission mixture.

Finally, we have studied the nitration of 2 : 4-dichlorophenyl benzoate, and found that this substance, when dinitrated, gives 2 : *4-dichloro-5-nitrophenyl m-nitrobenzoate*, accompanied apparently by traces of the *o*- and *p*-nitrobenzoates, but unaccompanied by the 3- or the 6-nitro-compound. For the *benzoate* of 2 : 4-dichloro-5-nitrophenol is nitrated to give a product of the same composition, and the main constituent of either nitration product is identical with the product of the *m*-nitrobenzoylation of 2 : 4-dichloro-5-nitrophenol, but distinct from 2 : *4-dichloro-6-nitrophenyl* m-*nitrobenzoate*.

The monohalogenation of *m*-nitrophenol and the nitration of ethers analogous to those described above are under investigation.

EXPERIMENTAL.

Preparation of 2 : 4-*Dichlorophenol*.—We have found that this substance is most readily obtained from *p*-chlorophenol. Chlorine was passed into a cooled solution of 128·5 g. of the latter substance in 500 c.c. of glacial acetic acid, until the required increase in weigh was obtained. The product was then distilled, and 129 g. of 2 : 4 dichlorophenol (b. p. 209—211°) were obtained (yield, 80%) *o*-Chlorophenol may be used instead of *p*-chlorophenol.

2 : 4-*Dichlorophenyl* p-*toluenesulphonate* is readily formed by th normal method, and crystallises from alcohol in rhombohedra prisms, m. p. 125° (Found: Cl, 22·4. $C_{13}H_{10}O_3Cl_2S$ require Cl, 22·4%).

Nitration of 2 : 4-*Dichlorophenyl* p-*Toluenesulphonate*.—The su phonate (30 g.) was added in small quantities to 300 c.c. of nitr acid (*d* 1·5), with water-cooling. After 30 minutes, the solutic was poured on ice, and the resulting solid washed with boili water. 2 : 4-*Dichloro-5-nitrophenyl* o-*nitro*-p-*toluenesulphona* separates from alcohol in colourless prisms, m. p. 103° (Foun Cl, 17·3. $C_{13}H_8O_7N_2Cl_2S$ requires Cl, 18·0%).

2 : 4-*Dichloro-5-aminophenyl* o-*Amino*-p-*toluenesulphonate*.—T preceding dinitro-compound was reduced by iron powder, wat and a little acetic acid. The *diamino*-compound forms colourl tooth-shaped needles from alcohol–acetone, and has m. p. 159—16 (Found: Cl, 19·8. $C_{13}H_{12}O_3N_2Cl_2S$ requires Cl, 20·4%); it diazotised readily, and the resulting solution couples normally w β-naphthol. The base does not condense with salicylaldehyde boiling alcoholic solution, but does so at the b. p. of the aldehyde

Isolation of 2 : 4 : 5-*Trichlorophenol*.—The diamino-compound v diazotised in dilute hydrochloric acid, the resulting solution be added to cuprous chloride–hydrochloric acid. After nor

procedure, the tetrachloro-sulphonate was obtained as a red gum, which was not further purified. It was heated under reflux for 3 hours with piperidine. The resulting solution was then rendered strongly acid, and distilled in a current of steam. The oil passing over solidified on cooling, and had m. p. 66—67° (Found : Cl, 54·2. Calc. : Cl, 54·0%). 2 : 4 : 5-Trichlorophenol forms a sparingly soluble potassium salt. The benzoate obtained from our specimen of the phenol melted at 91—92° (compare Holleman, *loc. cit.*).

Chlorination of 2 : 5-*Dichlorophenol.*—The phenol was dissolved in three times its weight of glacial acetic acid, in which the necessary amount of anhydrous sodium acetate had previously been dissolved. Chlorine was passed through the cooled solution until the required increase in weight was obtained, and water was then added. The precipitated 2 : 4 : 5-trichlorophenol was purified by sublimation, and then had m. p. 66—67°. The benzoate melted at 91—92°.

Preparation of 2 : 4 : 5-*Trichlorophenol from* 2 : 4 : 5-*Trichloroaniline.*—This was satisfactorily effected by the method described by Noelting and Kopp (*Ber.*, 1905, **38**, 3506) for the conversion of 2 : 5-dichloroaniline into 2 : 5-dichlorophenol. The specimen of trichlorophenol obtained had m. p. 66—67° (benzoate, m. p. 91—92°). Mixtures of any two of the various preparations of trichlorophenol also melted at 66—67°.

1-p-*Toluenesulphonylpiperidine and* 1-o-*Nitro*-p-*toluenesulphonylpiperidine.*—Piperidine readily reacted with *p*-toluenesulphonyl chloride or with its *o*-nitro-derivative in aqueous alkaline suspension. 1-*p*-*Toluenesulphonylpiperidine* crystallises from alcohol in colourless needles, m. p. 103° (Found : S, 13·7. $C_{12}H_{17}O_2NS$ requires S, 13·4%). 1-o-*Nitro*-p-*toluenesulphonylpiperidine* ›parates from alcohol in pale greenish-yellow prisms, m. p. 112° Found : S, 12·4. $C_{12}H_{16}O_4N_2S$ requires S, 12·1%).

Action of Piperidine on 2 : 4-*Dichloro-5-nitrophenyl* o-*Nitro*-p-*luenesulphonate.*—The latter compound was heated with one-ıird of its weight of piperidine for 1·5 hours at 100°. No separation f piperidine hydrochloride occurred, showing that hydrolysis of the ılphonate group takes place much more rapidly than replacement f chlorine. The red solution was treated with dilute alkali, and the il which separated soon became solid, and after crystallisation om alcohol had m. p. 112° either alone or when mixed with a ›ecimen of synthetic 1-*o*-nitro-*p*-toluenesulphonylpiperidine. The lkaline mother-liquor was acidified, and the resulting precipitate ›crystallised from water (Found : Cl, 34·1. $C_6H_3O_3NCl_2$ requires l, 34·1%). 2 : 4-*Dichloro-5-nitrophenol* forms almost colourless eedles, m. p. 105—106°. The potassium salt is sparingly soluble.

N-2 : 4-*Dichlorophenylphthalimide*.—2 : 4-Dichloroaniline (132 g.) was treated with powdered phthalic anhydride (124 g.), and the mixture heated at 200° for an hour. The still molten material was poured into 300 c.c. of cold alcohol, and when the resulting solution cooled, the required *phthalimide* crystallised out. It was recrystallised from alcohol, and then formed colourless prisms, m. p. 155° (Found : Cl, 24·4. $C_{14}H_7O_2NCl_2$ requires Cl, 24·3%) (yield, 195 g.).

2 : 4-*Dichloro-5-nitroaniline*.—To a solution of 190 g. of the dichlorophenylphthalimide in 1 litre of concentrated sulphuric acid were slowly added 34·5 c.c. of nitric acid (*d* 1·5), the temperature being kept below 30°. The solution obtained was poured on ice, and the precipitate collected and washed (208 g.). N-2 : 4-*Dichloro-5-nitrophenylphthalimide* crystallises from *cyclo*hexanone in pale yellow octahedra, m. p. 217—219° (Found : Cl, 20·8. $C_{14}H_6O_4N_2Cl_2$ requires Cl, 21·1%). The phthalimide (200 g.) was heated at 120° for 30 minutes with 1 litre of 90% sulphuric acid, the solution was cooled, poured into excess of ammonia containing ice, and the precipitated base collected. After purification it had the properties recorded by Körner and Contardi (*loc. cit.*) (Found : Cl, 34·3. Calc. : Cl, 34·3%). It was found impossible to prepare the base by nitrating 2 : 4-dichloroaniline in excess of concentrated sulphuric acid at −15°.

Diazo-solutions obtained from the base in either dilute or concentrated hydrochloric acid, or in dilute or moderately concentrated sulphuric acid, were heated under a variety of conditions. In two cases copper sulphate was added, but in no case could 2 : 4-dichloro-5-nitrophenol be isolated.

2 : 4-*Dichloro-2′ : 4′-dinitrodiphenyl Ether*.—When 40 g. of 1-chloro-2 : 4-dinitrobenzene were added to a solution of 32 g. of 2 : 4-dichlorophenol in 11 g. of potassium hydroxide, previously dissolved hot in about 0·5 c.c. of water, rapid interaction occurred, and after the mixture had been kept at 100° for ½ hour, water was added. The solid obtained was ground with dilute alkali solution and washed with water. It crystallised from glacial acetic acid in very pale greenish-yellow leaflets, m. p. 118—119° (Found Cl, 21·6. $C_{12}H_6O_5N_2Cl_2$ requires Cl, 21·6%).

Nitration of 2 : 4-*Dichloro-2′ : 4′-dinitrodiphenyl Ether*.—10 G. of the ether were added slowly to 100 c.c. of nitric acid (*d* 1·5) without cooling. After one hour, the clear solution was poured into excess of water. The resulting precipitate crystallised from 90% acetic acid in colourless rhombohedra, m. p. 128° (Found Cl, 18·9. $C_{12}H_5O_7N_3Cl_2$ requires Cl, 19·1%).

Scission of 2 : 4-*Dichloro-5 : 2′ : 4′-trinitrodiphenyl Ether*.—(a) *With piperidine*. A mixture of 18·5 g. of the trinitro-compound

with 22 g. of piperidine was heated at 100° for 2 hours. No piperidine hydrochloride separated. The solution was diluted and rendered strongly alkaline, and the precipitated 2 : 4-dinitrophenylpiperidine was collected and extracted with benzene until no more coloured product was removed. The aqueous solution was freed from benzene by heating at 100°, cooled, and slowly acidified. The almost colourless precipitate was dried, and crystallised from light petroleum (b. p. 80—100°). The resulting product melted at 105—106° either alone or when mixed with the 2 : 4-dichloro-5-nitrophenol obtained from the above toluenesulphonate.

When a chloroform solution of either 1 or 2 mols. of piperidine was added slowly to a boiling solution of the dichlorotrinitro-compound (1 mol.), scission was quantitatively effected.

(*b*) *With aniline.* A solution of 20 g. of the dichlorotrinitro-compound in 150 g. of aniline was heated for 4 hours at 100°. The solution was shaken with hydrochloric acid, and the resulting reddish precipitate filtered off; it was identical with a pure specimen of 2 : 4-dinitrodiphenylamine, and was obtained in theoretical yield. When the filtrate became cool, 2 : 4-dichloro-5-nitrophenol, containing a little dinitrodiphenylamine and considerable aniline hydrochloride, separated and was filtered off. After removal of aniline hydrochloride by washing with cold water, the phenol was purified by dissolution in dilute alkali, filtration, and precipitation with dilute acid.

4 : 4′-*Dichloro-2-nitrodiphenyl Ether.*—The following method was found much more satisfactory than existing methods, *e.g.*, that of Raiford and Colbert (*J. Amer. Chem. Soc.*, 1926, **48**, 2652): *p*-Dichlorobenzene (100 g.) was added within 15 minutes to 500 g. of nitric acid (*d* 1·5). After a further 15 minutes, the solution was poured into excess of cold water, and the precipitated solid air-dried. The whole was introduced into a solution obtained by adding 88 g. of *p*-chlorophenol to 37 g. of potassium hydroxide which had previously been heated to a clear melt in presence of 1—2 c.c. of water. The mixture was heated in a bath kept at 160—170° for 2 hours, cooled, and shaken with dilute alkali until the precipitated material (162 g.) was crystalline. After one crystallisation from alcohol, the nitro-compound was pure. Use of copper bronze does not increase the yield, and hampers manipulation; moreover, it apparently causes formation of some 4-chloro-4′-hydroxydiphenyl ether.

4 : 4′-*Dichloro-2-aminodiphenyl Ether.*—The nitro-compound was reduced at 100° by means of iron filings and excess of water in presence of a little acetic acid. The crude base, produced in 90% of the theoretical yield, crystallises from light petroleum (b. p. 80—100°)

This was nitrated as above, and gave a product identical in properties with that obtained from 2 : 4-dichlorophenyl benzoate.

The m-*nitrobenzoate* of 2 : 4-dichlorophenol crystallises from alcohol in hairy needles, m. p. 115—116° (Found: Cl, 23·3. $C_{13}H_7O_4NCl_2$ requires Cl, 22·8%). Nitration of this product gave pure 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate, m. p. 154°. An identical substance was obtained by condensing 2 : 4-dichloro-5-nitrophenol with *m*-nitrobenzoyl chloride in warm alkaline suspension.

2 : 4-*Dichloro*-6-*nitrophenyl* m-*nitrobenzoate*, prepared for comparison purposes from the product of dichlorinating *o*-nitrophenol (Tarugi, *Gazzetta*, 1891, **30**, 491), is very sparingly soluble in alcohol, from which it crystallises in colourless prisms, m. p. 149—150° (Found: Cl, 19·5%). A mixture of this substance with 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate melted at 128—129°.

Chlorination of m-*Nitrophenol*.—Chlorine was passed into 20 g. of *m*-nitrophenol, which was kept just liquid by heating. When the calculated increase in weight was obtained the 2 : 4-*dichloro*-3-*nitrophenol* (see below) was twice crystallised from light petroleum (b. p. 80—100°). It formed very pale yellowish-green needles, m. p. 70—72°, raised to 85—87° after drying in a vacuum over sulphuric acid (Found: Cl, 34·1. $C_6H_3O_3NCl_2$ requires Cl, 34·1%).

The p-*toluenesulphonyl* derivative crystallised from alcohol in leaflets, m. p. 122° (Found: Cl, 19·3; S, 9·5. $C_{13}H_9O_5NCl_2S$ requires Cl, 19·6; S, 8·8%); it was reduced by means of iron, water, and a little acetic acid to 2 : 4-*dichloro*-3-*aminophenyl* p-*toluenesulphonate*, which crystallised from light petroleum (b. p. 80—100°) in colourless plates, m. p. 113—114° (Found: Cl, 21·4; S, 9·5. $C_{13}H_{11}O_3NCl_2S$ requires Cl, 21·9; S, 9·6%).

The amino-compound is apparently unaffected by hot concentrated hydrochloric acid, the resulting suspension after being cooled no undergoing diazotisation to any appreciable extent. Replacemen of the amino-group by chlorine was therefore effected as follows A solution of 9 g. of the amino-compound in 30 c.c. of concentrate sulphuric acid was diazotised at 20° with a solution of 2 g. of sodiu nitrite in 15 c.c. of concentrated sulphuric acid, prepared at −15 The clear solution obtained by pouring on ice was added to cuprou chloride–hydrochloric acid, and the resulting mixture was distille in steam. The crude solid which passed over was dissolved i excess of piperidine and the solution was boiled under reflux for a hour, then strongly acidified, and distilled in steam. Almost pu 2 : 3 : 4-*trichlorophenol* passed over. It was purified by dissoluti in alkali, followed by acidification, and finally by sublimation. forms colourless needles, m. p. 80—81° (Found: Cl, 54·8. C_6H_3OC

requires Cl, 54·0%). The benzoate had m. p. 143° (compare Holleman, *loc. cit.*).

Chlorination of 3 : 4-*Dichlorophenol*.—This phenol was readily obtained by application of the method of Noelting and Kopp (*loc. cit.*). Chlorination was carried out as in the case of 2 : 5-dichlorophenol (p. 517). The sample of 2 : 3 : 4-trichlorophenol was in no way different from that described above, and gave a benzoate of m. p. 143° (Found: Cl, 35·2. Calc.: Cl, 35·3%), unaltered on admixture with the benzoate described above.

Action of Phosphorus Pentachloride and of Thionyl Chloride on 2 : 4-*Dichloro*-5-*nitrophenol*.—In preliminary attempts to establish the identity of this phenol, it was heated with 2 parts (= 2 mols.) of phosphorus pentachloride at 150—160° for 1·5 hours. The cooled product was extracted with carbon tetrachloride, and the extract well washed with alkali. Removal of the solvent gave a product, b. p. 150—160°/15 mm., m. p. 80—89°, but insufficient was obtained for detailed examination.

The dichloronitrophenol crystallises unchanged from thionyl chloride even after prolonged boiling of the solution.

4 : 5-*Dichloro*-2-*nitrodiphenyl Ether*.—4 : 5-Dichloro-1 : 2-dinitrobenzene (1 mol.) was added to a solution of potassium phenoxide (1 mol.) in the minimum amount of water. A brown-red coloration appeared, and rapidly faded. Completion of the condensation was effected by heating at 100° for ½ hour and the *ether*, after being washed with alkali, became solid, and then crystallised from alcohol in yellow prisms, m. p. 69—70° (Found: Cl, 24·8. $C_{12}H_7O_3NCl_2$ requires Cl, 25·0%).

4 : 5 : 4′-*Trichloro*-2-*nitrodiphenyl ether* was similarly obtained from potassium *p*-chlorophenoxide. It separates from alcohol in very pale yellow needles, m. p. 77° (Found: Cl, 32·8. $C_{12}H_6O_3NCl_3$ requires Cl, 33·4%). When the ether was dissolved in 20 parts of nitric acid (*d* 1·5), the temperature rose appreciably, and after 10 minutes crystallisation set in. The whole was poured on ice, and the precipitate was crystallised from alcohol. 4 : 5 : 4′-*Trichloro*-2 : 2′-*dinitrodiphenyl ether* forms very pale yellow, hairy needles, m. p. 131—132° (Found: Cl, 29·0. $C_{12}H_5O_5N_2Cl_3$ requires Cl, 29·2%). Boiling piperidine converted this substance into a mixture, the alkali-insoluble portion being 4-chloro-2-nitrophenylpiperidine. This establishes the constitution of the ether.

4 : 5 : 2′ : 4′-*Tetrachloro*-2-*nitrodiphenyl ether*, obtained from 4 : 5-dichloro-1 : 2-dinitrobenzene and potassium 2 : 4-dichlorophenoxide, crystallises from alcohol in pale yellow leaflets, m. p. 125—126° (Found: Cl, 40·1. $C_{12}H_5O_3NCl_4$ requires Cl, 40·2%).

Reduction of the tetrachloronitro-ether by the iron method gave

4 : 5 : 2′ : 4′-*tetrachloro-2-aminodiphenyl ether*, crystallising from light petroleum (b. p. 80—100°) in colourless needles, m. p. 97—98° (Found: Cl, 43·9. $C_{12}H_7ONCl_4$ requires Cl, 43·9%). Attempted replacement of the amino-group by chlorine proved unsuccessful.

Part of the expense of this investigation was met by grants from the Research Fund of the Chemical Society.

East London College,
University of London. [*Received, December 31st*, 1928.]

LXXVII.—*The Enzymic Synthesis of β-Hydroxyethyl Dihydrogen Phosphate.*

By Herbert Davenport Kay.

As yet, the number of cases in which the reversible activity of an enzyme * derived from plant or animal tissues has been clearly demonstrated *in vitro* by the isolation in a pure form of the synthesised product of the reaction, is small. The demonstration of such synthetic activity has considerable importance both with regard to the theory of catalysis and in connexion with the rôle played by the particular enzyme in the life processes of the tissue from which it is derived.

Using the very active phosphoric esterase of the intestinal mucosa as a catalyst, I have shown (*Biochem. J.*, 1928, **22**, 855) that sodium glycerophosphate may be readily synthesised at 37° from sodium phosphate and glycerol if the concentration of water in the reaction mixture is kept sufficiently low. The synthesised ester may be conveniently isolated as the alcohol-insoluble barium salt.

The production, by the same esterase, of a phosphoric ester from ethylene glycol will now be described, and details with regard to its composition and properties will be given which show its identity with the hydroxyethyl phosphoric ester derived from the product of the direct combination between ethylene chlorohydrin and phosphoryl chloride (Plimmer and Burch, this vol., p. 284).

Experimental.

Commercial ethylene glycol was twice distilled, the portion of b. p. 193—195° (uncorr.) being used. An extract of the duodenal mucosa of a cat was prepared by carefully washing out the intestine with water, scraping off the mucosa of the duodenum, and grinding

* The first definitely proved case of enzymic synthesis was recorded by Croft Hill (J., 1898, **73**, 634).

a weighed quantity of the wet tissue with washed sand and water containing a little chloroform. The extract was made up to twenty times the original weight of mucosa with water.

Ten g. of disodium hydrogen phosphate crystals were dissolved in 75 c.c. of this extract, and 200 c.c. of the redistilled glycol added. A sample was taken at once from the slightly alkaline reaction mixture, and inorganic and total phosphorus were determined in it. The determinations were repeated at intervals (Table I).

TABLE I.

Rate of synthesis of the ester.

Time (days).	Mg. of P per c.c. of reaction mixture. Inorganic P.	Total P.	Combined (ester) P.
0	3·27	3·31	0·04
3	2·55	3·30	0·75
6	2·38	3·31	0·93
10	2·22	—	1·09
15	2·13	—	1·18
17	2·08	3·31	1·23
21	2·06	3·27	1·21

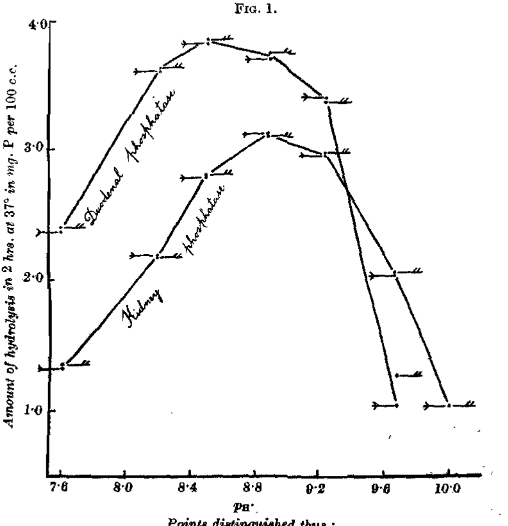
Controls with boiled enzyme showed no synthesis whatever in 21 days.

At this stage the reaction had evidently almost reached equilibrium. The reaction mixture (262 c.c.), containing 317 mg. P of esterified phosphate, was placed in a boiling water-bath for 10 minutes to inactivate the enzyme and then cooled. This treatment produced no rise in the inorganic phosphate. Barium nitrate (8 g. in 50 c.c. of water) was added, followed by barium hydroxide solution until the whole was a faint pink to phenolphthalein. All the inorganic and most of the combined phosphorus were thus precipitated (ppt. A), but there still remained 77 mg. of esterified P in the filtrate. This was precipitated as the lead salt, which was washed twice with water and decomposed by hydrogen sulphide, and the solution after aeration was neutralised with sodium hydroxide. The lead precipitation was repeated once more in dilute acetic acid with lead acetate. After removal of the lead, the aerated filtrate was neutralised with warm barium hydroxide solution, filtered, and treated with 2 volumes of 98% alcohol. The precipitated barium salt was washed with 60% alcohol, dissolved in water containing a little dilute acetic acid, again precipitated by addition of an equal volume of 98% alcohol, washed, and dried at 110° (0·40 g. Product B).

The main amount of esterified phosphate was still in ppt. A. This was ground with dilute acetic acid and filtered: the whole of the combined phosphorus was found in the solution (220 mg.) together with 20 mg. of inorganic phosphate.

20 C.c. of 25% lead acetate solution were added to the faintly acid filtrate, and the precipitated lead salt was washed and decomposed in the usual way. The barium salt was now prepared, and precipitated by alcohol. It was transformed again into the lead salt, and finally the purified barium salt was precipitated twice by an equal volume of alcohol, obtained in micro-crystalline form from warm aqueous alcohol, and dried at 100° over phosphoric oxide

FIG. 1.



Points distinguished thus :
Enzymically synthesised ester ➝—• *"Chemically" synthesised ester* •—//

(yield, 1·6 g. Product C) (Found in product B: Ba, 50·3; P, 11·25. Found in product C: Ba, 49·7, 49·9; P, 11·3, 11·4. Calc. for barium hydroxyethyl phosphate, $HO\cdot C_2H_4\cdot O\cdot PO_3Ba$: Ba, 49·5; P, 11·2%).

Through the kindness of Prof. R. H. A. Plimmer and Mr. W. T. J. Burch, who provided me with a sample of barium hydroxyethyl phosphate prepared by purely chemical means, I was able to obtain further evidence confirming the identity of the chemically and the

biochemically synthesised substance as follows. The two barium salts were dissolved separately in water and decomposed by the theoretical quantity of sodium sulphate solution. The filtrates were diluted to contain 0·300 mg. P per c.c. Preliminary experiments having shown that the optimum p_H for the enzymic hydrolysis of the glycophosphate was between 8·0 and 9·0, 5 c.c. portions of the two solutions were run into two series of test-tubes, containing 5 c.c. of borate or glycine buffers to cover a p_H range from 7·6 to 10·0.

In one series 0·5 c.c. of a solution containing kidney phosphatase, and in the other 0·5 c.c. of the same duodenal extract which catalysed the synthesis, were then added to each tube, and the amount of hydrolysis of the ester after a period of 2 hours at 37° was determined in each series, the Briggs method (*J. Biol. Chem.*, 1922, **53**, 13) of phosphate determination being used. Adequate controls were made in each series.

The results are shown in Fig. 1, which indicates clearly that the two substrates are hydrolysed (*a*) at the same optimal p_H, (*b*) at the same rate, by the same enzyme solution. (The optimum is not quite the same for the two widely different enzyme preparations.) A solution of sodium β-glycerophosphate submitted to the action of the same enzyme preparations under identical conditions showed a considerably higher rate of hydrolysis.

THE MEDICAL UNIT,
LONDON HOSPITAL. [*Received, January 3rd*, 1929.]

LXXVIII.—*The Boric Acids.*

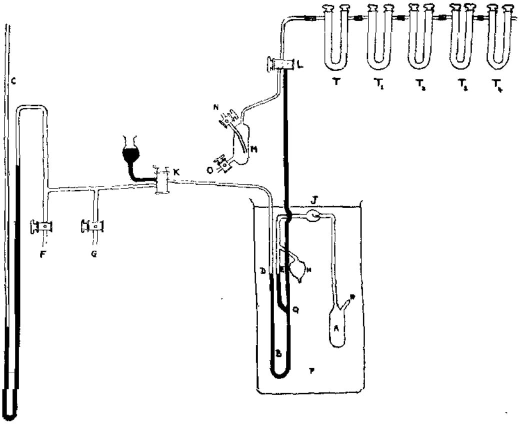
By LIONEL FELIX GILBERT and MIRIAM LEVI.

SEVERAL compounds of boric anhydride with water in various proportions have been reported, but examination of the original literature shows that in many cases the experimental evidence for their existence is inadequate. When the work now described was commenced, the following statement by Little (Friend's "Textbook of Inorganic Chemistry," Vol. IV) seemed to be well justified: "At the present time, the existence in the solid state of only two of the boric acids, orthoboric acid, H_3BO_3 (*i.e.*, $B_2O_3,3H_2O$), and metaboric acid, HBO_2 (*i.e.*, B_2O_3,H_2O), can be definitely affirmed."

It was decided to attempt to solve the problem by a method similar to that commonly employed in investigating a series of salt hydrates, *viz.*, by combining determinations of vapour pressures in the system B_2O_3–H_2O with measurements of weights of water lost in passing from one part of the system to another.

After a number of trials, an apparatus of the type shown in Fig. 1 (which is not to scale) was evolved. Considered from the point of view of pressure measurements it is similar to that employed by Caven and Sand (J., 1911, **99**, 1359), but differs in that it has provision for the withdrawal and quantitative collection of water vapour. The apparatus thus modified is very suitable for the examination of many types of equilibria such as those described here.

FIG. 1.



The bulb, A, containing the mixture under examination is connected through the mercury gauge, B, maintained at the same temperature, to the manometer, C; when the levels of the mercury in the limbs, D and E, of the mercury gauge are the same, the pressure in A can be read directly at C. The taps, F and G, are connected respectively to a pump and to the atmosphere *via* a drying tube, so the pressure in the apparatus, and consequently the levels in D and E, can be adjusted as required. H is a bulb which is of use when the pressure in A decreases during experiments preventing mercury from running back into A. A further safety trap, J, is provided. Mercury can be introduced at the three-way tap, K. The special form of the mercury gauge allows water vapour to be removed at the tap L, which is connected through a mercury

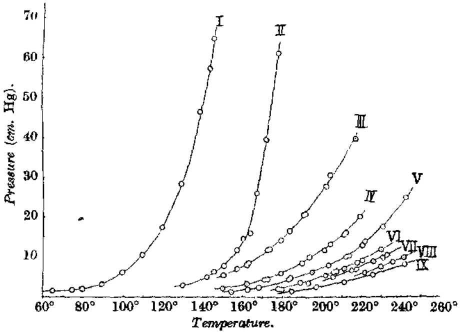
trap, T, to a series of weighed drying tubes, T_1, T_2, etc., the first containing calcium chloride and the remainder phosphoric oxide. The last drying tube is connected through a guard tube to a Hyvac pump. It was found possible to dispense with some of the drying tubes in the later stages of the experiments, where little water was evolved. L can be put into communication also with a trap, M, connected at N to calcium chloride towers; this enables a stream of dry air to be drawn through the apparatus above L, thus accelerating the transfer of water to the drying tubes. A tap, O, is provided for withdrawing mercury, which from time to time falls into M when it is connected to the drying tubes.

Heating was effected by means of electrically heated B.P. paraffin in a 5-litre beaker, P, stirred by an electrically driven paddle placed in the centre. A modified form of thermo-regulator described by Lewis and Wood (*Trans. Faraday Soc.*, 1921, **17**, 696) was used. Temperature was measured by a glass–mercury thermometer with the bulb close to A. The bath liquid was not entirely satisfactory, for at temperatures above 100° it darkened rapidly, eventually becoming so black that it was impossible to continue reading the mercury gauge. Fresh oil had therefore to be substituted from time to time.

The experimental procedure was as follows. A known weight of powdered boric acid was placed in A, through the side-tube, R, which was then sealed off, after which the apparatus was evacuated at room temperature through the tap F. Mercury was then run in at K until the side-tube at Q was sealed, the levels in D and E being the same. The bath was then heated to a suitable temperature, the water vapour evolved exerting a pressure which eventually depressed the mercury in E to Q, thus allowing the vapour to pass up the tube QL. A small quantity of vapour (which was afterwards collected in the drying tubes) was withdrawn from A in this way in order to help to remove any adsorbed atmospheric gas still remaining which had not been removed during the initial evacuation at the lower temperature. When sufficient vapour had been withdrawn, the mercury was raised above Q by suitable manipulation of the taps F and G, and the levels D and E were kept approximately equal until equilibrium resulted. A careful adjustment of the levels was then made, and the pressure was read at C. To ensure that equilibrium had been attained, the pressure was allowed to remain constant for at least ½ hour before the decisive reading was taken. (This period sufficed for the higher hydrates, but not for the lower hydrates, where the attainment of equilibrium was much slower.) In many cases, further to ensure that equilibrium had been attained, the temperature of the bath was raised by 1—2° and then allowed to

revert to the temperature under consideration. The temperature was then raised by 10° steps, approximately, a series of points upon curve I in Fig. 2 thus being obtained, after correction for the vapour pressure of mercury, for which Ramsay and Young's values (J., 1886, 49, 37) were used. The temperature range was then similarly traversed in the reverse direction. Equilibrium was thus approached from both high and low temperatures. To proceed to the next hydrate system, a suitable temperature was selected, and equilibrium allowed to take place. The pressure in E was then lowered so that vapour from A could escape through Q and rise up through the mercury in the tube QL. Much of the water condensed at the top

FIG. 2.



of the tube, which was relatively cool. When sufficient water hac been removed from the system, the mercury level in E was raise(above Q to prevent any more vapour from escaping. The tap] was then opened to allow the water in the top of the mercury colum to pass through, together with a small quantity of mercury. (Wit very low pressures the mercury did not rise as far as L.) L we then turned so that the tubes T, T_1, etc., were in connexion with M and a current of dry air was pumped through so that all the wat was conveyed to the tubes, which were then reweighed. Th process was repeated until a sudden definite decrease in the pressu exerted by the contents of A was observed, after sufficient time h been allowed for equilibrium to be established. Water vapour w then slowly removed from A, a few bubbles at a time, until a n system resulted such that the withdrawal of a small quantity

water vapour had no effect on the equilibrium vapour pressure at constant temperature, *i.e.*, the vapour pressure was that of a new pair of hydrates of boric anhydride. The pressure–temperature curve for this system was determined, thus giving curve II. The other curves in Fig. 2 and the losses in weight on passing from one part of the system to the other were determined similarly.

Several runs were necessary, for, in spite of its having been carefully annealed, the apparatus frequently broke, possibly owing to the fact that glass tends to be attacked by boric oxide at the higher temperatures employed. In no case was it found possible to continue until complete dehydration was effected. In the last run that was carried out, however, as much as 97·5% of the water present in the initial orthoboric acid was removed before the experiment had to be discontinued.

Table I shows the data from which the pressure–temperature curves were constructed. Pressures (p) were read to the nearest mm.; temperatures (t) were usually constant to at least 0·5° during the course of individual experiments and were subject to emergent stem corrections, which would normally act in the same direction, but were not applied. The thermometers were checked against Anschütz thermometers, with which they agreed fairly closely. No high degree of accuracy is therefore claimed for these measurements, which were made with the primary object of obtaining definite indications of equilibrium.

In the most complete run that was made, the initial weight of orthoboric acid was 5·4856 g. and the amounts of water lost to bring the system on the curves II, III, . . . IX, successively were:

>1·5855<1·6591 g. (1·5926; n = 1)	>2·2295<2·2331 g. (2·2296; n = 5)
>1·9835<1·9925 g. (1·9907; n = 2)	>2·2541<2·2577 g. (2·2562; n = 6)
>2·1201<2·1267 g. (2·1234; n = 3)	>2·2663<2·2753 g. (2·2751; n = 7)
>2·1863<2·1923 g. (2·1898; n = 4)	>2·2753<2·2920 g. (2·2893; n = 8)

The figures in parentheses show the calculated loss of weight for the formation of the hydrate indicated by the value of n in the formula nB_2O_3,H_2O. The existence of these compounds is confirmed by similar data in a previous experiment from HBO_2 as far as $6B_2O_3,H_2O$, at which stage the apparatus broke.

The calculated losses in weight of water are subject to corrections for the mass of water vapour contained in the bulb A; these corrections become smaller as the more dehydrated products form, with their relatively low vapour pressures, and are never large enough to invalidate the main conclusions.

To obtain the theoretically exact figures, a further correction would be necessary on account of the volatilisation of the boric anhydride component, of which there was evidence from the form-

TABLE I.

I. $B_2O_3,3H_2O$–B_2O_3,H_2O.

t ...	65°	75°	80°	89·5°	99·5°	109·5°	119·5°	129°	139°
p ...	1·75	1·88	2·15	3·45	6·2	10·6	17·4	28·2	46·2
t ...	144°	146°							
p ...	57·1	64·6							

II. B_2O_3,H_2O–$2B_2O_3,H_2O$.

t ...	130°	142°	146·5°	150·5°	157°	160°	162°	167°	172°
p ...	3·0	4·9	6·2	7·8	11·35	14·5	16·95	25·7	39·25
t ...	178°								
p ...	60·8								

III. $2B_2O_3,H_2O$–$3B_2O_3,H_2O$.

t ...	150·5°	157°	162°	163°	172·5°	173·5°	179·5°	183·5°	191°
p ...	5·4	7·15	8·05	8·5	11·65	11·85	14·05	16·25	20·25
t ...	192°	202·5°	204·5°	218°					
p ...	20·5	27·3	30·3	39·5					

IV. $3B_2O_3,H_2O$–$4B_2O_3,H_2O$.

t ...	150°	162°	171°	172·5°	179·5°	179·5°	190°	194°	201·5°
p ...	2·3	3·25	4·1	4·35	5·65	5·75	8·1	9·7	11·4
t ...	204·5°	211·5°	212°	219·5°					
p ...	13·05	15·4	15·8	20·0					

V. $4B_2O_3,H_2O$–$5B_2O_3,H_2O$.

t ...	154·5°	163°	168·5°	183·5°	184·5°	195·5°	203·5°	212·5°	212·5°
p ...	1·5	1·95	2·2	4·35	4·7	6·0	7·8	9·9	9·5
t ...	214°	220·5°	222°	231°	231°	242·5°			
p ...	10·0	12·6	13·6	17·4	17·5	24·5			

VI. $5B_2O_3,H_2O$–$6B_2O_3,H_2O$.

t ...	178·5°	189°	202·5°	206°	207·5°	211·5°	218°	220·5°	230°
p ...	2·0	3·4	5·3	6·0	6·05	6·85	8·3	8·75	11·6

VII. $6B_2O_3,H_2O$–$7B_2O_3,H_2O$.

t ...	180°	193·5°	205·5°	215·5°	217·5°	226·5°	231°	233°
p ...	1·75	3·4	4·75	6·3	6·6	8·85	9·8	10·3

VIII. $7B_2O_3,H_2O$–$8B_2O_3,H_2O$.

t ...	222°	230°	236°	241·5°
p ...	5·8	7·3	8·5	9·0

IX. $8B_2O_3,H_2O$–B_2O_3(?).

t ...	185°	197·5°	211·5°	226°	246°
p ...	1·4	2·25	3·45	5·2	8·0

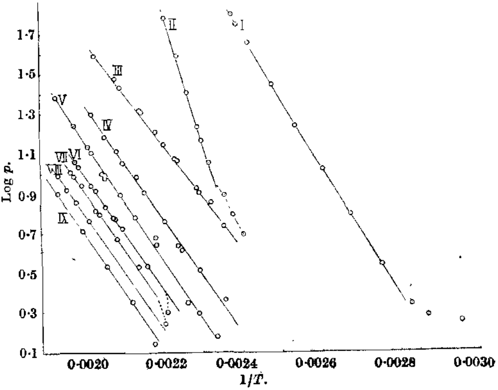
ation of a small quantity of a white deposit on the cooler parts of the tube QL, and also in T, but not in the exit tube of T. Most of this volatilisation seemed to occur when curves I and II were being examined. In one case when a breakage happened after 95·2% of the water had been removed, it was possible to obtain the contents of the bulb A in a clean state and to determine the boric oxide content, which was found to be more than 99% of that originally present. As most of this oxide condensed in the tube QL, it could retain relatively little water owing to the high temperature to which it was still subjected, and to the fact that it was in the form of a thin film which would facilitate the establishment of the boric

anhydride–water equilibrium. It does not appear, therefore, that the volatilisation of the boric anhydride component affects materially the data under consideration.

Curves I to VIII correspond therefore to equilibria between water vapour and the systems $B_2O_3,3H_2O$–B_2O_3,H_2O; B_2O_3,H_2O–$2B_2O_3,H_2O$; . . . $7B_2O_3,H_2O$–$8B_2O_3,H_2O$.

It is not impossible that still lower hydrates of boric anhydride exist, but since, in the case in which 97·5% of the water was withdrawn, the vapour pressures exerted were still on curve IX, whereas the removal of 95·8 and 96·3% of water corresponds with the

Fig. 3.



formation of $8B_2O_3,H_2O$ and $9B_2O_3,H_2O$ respectively, it would seem that $9B_2O_3,H_2O$ cannot exist under our experimental conditions; if, therefore, curve IX does not represent the vapour-pressure curve for the system $8B_2O_3,H_2O$–B_2O_3, some hydrate lower than $9B_2O_3,H_2O$ is involved. Attainment of equilibrium is very slow, however, at this part of the system, and more data would be desirable.

A few measurements of the pressures exerted when orthoboric acid is heated at different temperatures are recorded by Lescoeur (*Ann. Chim. Phys.*, 1890, **19**, 35) and apparently belong to the system $3H_2O,B_2O_3$–H_2O,B_2O_3, as they are in rough agreement with our values for this system.

When the data of Table I are plotted as log p against $1/T$, Fig. 3

is obtained. It will be observed that the curves are approximately straight lines, with the exception of a few points at the lower tempertures (the deviations of which cannot be entirely explained). Hence the average approximate values of the heats of combination, Q, of the different hydrates (with one molecule of water vapour) can be calculated from the slopes of the lines by application of the equation $Q = 4{\cdot}576\, d \log p/d\,(1/T)$. The values of Q (in cals.) corresponding to the several curves are as follows: I, 15,600; II, 31,300; III, 12,300; IV, 13,300; V, 14,000; VI, 13,200; VII, 13,100; VIII, 13,500; IX, 13,300. From these are calculated the successive heat changes in the dehydration of orthoboric acid, as shown in Table II, the lowest hydrate capable of existence being assumed to be $8B_2O_3,H_2O$. *On this assumption the heat of hydration of boric oxide to orthoboric acid is 54,363 cals.*

Even if still lower hydrates exist, their contribution to the total heat of hydration would probably be small and of the same sign as in Table II. By subtracting the heat of vaporisation of three

TABLE II.

$B_2O_3,3H_2O$	$\longrightarrow B_2O_3,H_2O + 2H_2O$	$-$ 31,200	*cals.*
B_2O_3,H_2O	$\longrightarrow B_2O_3,\frac{1}{2}H_2O + \frac{1}{2}H_2O$	$-$ 16,650	,,
$\frac{1}{2}(2B_2O_3,H_2O)$	$\longrightarrow \frac{1}{3}(3B_2O_3,H_2O) + \frac{1}{6}H_2O$	$-$ 2,050	,,
$\frac{1}{3}(3B_2O_3,H_2O)$	$\longrightarrow \frac{1}{4}(4B_2O_3,H_2O) + \frac{1}{12}H_2O$	$-$ 1,108	,,
$\frac{1}{4}(4B_2O_3,H_2O)$	$\longrightarrow \frac{1}{5}(5B_2O_3,H_2O) + \frac{1}{20}H_2O$	$-$ 700	,,
$\frac{1}{5}(5B_2O_3,H_2O)$	$\longrightarrow \frac{1}{6}(6B_2O_3,H_2O) + \frac{1}{30}H_2O$	$-$ 440	,,
$\frac{1}{6}(6B_2O_3,H_2O)$	$\longrightarrow \frac{1}{7}(7B_2O_3,H_2O) + \frac{1}{42}H_2O$	$-$ 312	,,
$\frac{1}{7}(7B_2O_3,H_2O)$	$\longrightarrow \frac{1}{8}(8B_2O_3,H_2O) + \frac{1}{56}H_2O$	$-$ 241	,,
$\frac{1}{8}(8B_2O_3,H_2O)$	$\longrightarrow B_2O_3 + \frac{1}{8}H_2O$	$-$ 1,662	,,

molecules of water (27,650 cals.), the value 26,700 cals. (approx.) *is obtained*, which can be compared with the values determined calorimetrically by Ditte (12,509 cals.; *Ann. Chim. Phys.*, 1878, **13**, 70) and by Berthelot (16,800 cals; *ibid.*, 1879, **17**, 133). As Ditte employed for his determination powdered boric oxide, which must have absorbed a large amount of water during its preparation owing to its exceedingly hygroscopic nature, the discrepancy between his value and ours is explained. Although Berthelot does not state the fact, it seems most likely that the boric oxide he used was also powdered, for the fused material dissolves only very slowly, probably far too slowly for such calorimetric methods as he was able to apply and his determinations suffered, therefore, from the same error.

Summary.

Evidence is adduced for the existence of eight boric acids nB_2O_3,H_2O, where $n = 1, 2, 3 \ldots 8$. An approximate value fo the heat of hydration of boric anhydride to orthoboric acid i

advanced, and differs considerably from previous data, which are shown to be probably inaccurate.

THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, December 13th,* 1928.]

LXXIX.—*Observations on the Chlorination Products of ββ′-Dichlorodiethyl Sulphide. Part II.*

By JOHN WILLIAM COLE PHILLIPS, JOHN STANLEY HERBERT DAVIES, and STANLEY AUGUSTUS MUMFORD.

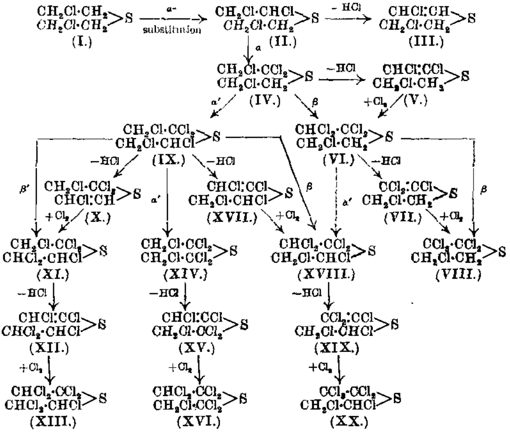
IN a previous paper (Mumford and Phillips, J., 1928, 155) the view was advanced that the products of chlorination of ββ′-dichlorodiethyl sulphide described by Mann and Pope (J., 1922, **121**, 594) as αββ′-trichloro- and αβββ′-tetrachloro-diethyl sulphides were αβ-dichloro- and αββ-trichloro-vinyl β-chloroethyl sulphides, respectively. Subsequent to the communication of that paper, but prior to its publication, two papers on the same subject appeared (Lawson and Dawson, *J. Amer. Chem. Soc.*, 1927, **49**, 3119, 3125) in which similar conclusions were reached concerning the unsaturated nature of these compounds.

The present investigation was undertaken primarily to confirm the views previously advanced, but continuation of the work has shown that the chlorination of ββ′-dichlorodiethyl sulphide gives rise, not only to the series of compounds containing an unchanged β-chloroethyl group, as described by Mann and Pope and by Lawson and Dawson, but also to a second series in which chlorination has occurred in both chloroethyl groups. The main result of our work is thus the isolation not only of the tri- and tetra-chlorinated ethyl vinyl sulphides and the hexachlorodiethyl sulphide of the above observers, but also of one, or possibly two, new tetrachlorinated ethyl vinyl sulphides, together with pentachlorinated ethyl vinyl sulphides, hexachlorodiethyl sulphides, and heptachlorodiethyl sulphides derived from them.

Chlorination of ββ′-Dichlorodiethyl Sulphide (I).

The experiments now recorded were restricted to the chlorination of ββ′-dichlorodiethyl sulphide with two or more molecules of chlorine, and as far as the production of β-chloroethyl αβ-dichlorovinyl (V) and αββ-trichlorovinyl sulphides (VII) from saturated polychlorodiethyl sulphides is concerned, our results agree with those of Lawson and Dawson. For from the results obtained (Table I), it is evident that ββ′-dichlorodiethyl sulphide, on treatment with

chlorine at the ordinary temperature, undergoes substitution, since for every molecule of chlorine used, one molecule of hydrogen chloride is evolved (Expts. 1 and 2). Moreover, each molecule of substitution product so formed breaks down on heating with the evolution of a further molecule of hydrogen chloride.



When one molecule of the dichloro-sulphide reacts with two molecules of chlorine (Expt. 7), the main reaction is the formation of a tetrachlorodiethyl sulphide (IV), which, however, is extremely unstable, and decomposes on attempted distillation, losing a molecular proportion of hydrogen chloride and giving in 90% yield an unsaturated trichloro-sulphide (V). We have not yet had an opportunity of examining the earlier stages of the chlorination process, but from the work of Lawson and Dawson it would appear that this tetrachlorodiethyl sulphide is the di-α-substituted derivative, and that the derived unsaturated trichloro-compound is β-chloroethyl αβ-dichlorovinyl sulphide (V). Confirmation of the existence of the vinyl chain in the latter is afforded by the fact that when the sulphide is treated with chlorine the principal reaction is one of addition, yielding ααββ'-pentachlorodiethyl sulphide (VI), which loses hydrogen chloride on heating to give β-chloroethyl αββ-trichlorovinyl sulphide (VII), in 70% yield (Expts. 13 and 14).

From this, by addition of chlorine, ααβββ′-hexachlorodiethyl sulphide (VIII) is obtained (Expts. 15 and 16), which, as might be expected from its constitution, yields hexachloroethane on further chlorination in the cold, and, like (V) and (VII), gives β-chloroethanesulphonic acid on oxidation (Mann and Pope ; Lawson and Dawson, *locc. cit.*).

When, however, ββ′-dichlorodiethyl sulphide is treated with more than two molecules of chlorine and the resulting pentachlorodiethyl sulphide is broken down with loss of hydrogen chloride, only on rare occasions is a tetrachlorinated ethyl vinyl sulphide identical with (VII) obtained. More often, an isomeric unsaturated tetrachloro-compound is produced, very similar to (VII) in physical properties but differing markedly from it in rate of hydrolysis. The sulphide (VII), when boiled with water for 15 minutes, is hydrolysed to the extent of 2% only, but with the new unsaturated tetrachloro-compound under similar conditions an apparent chlorine content of 70% is indicated. The compound, however, only contains 62·8% of chlorine, and, as estimation of the chloride formed shows that 59% is due to hydrogen chloride (*i.e.*, about 3·75 atoms of chlorine), it follows that the 70% figure corresponds to the liberation of about 0·75 mol. of acid in excess of that accounted for as hydrogen chloride.

As regards the genesis of this new compound, it would appear that just as ββ′-dichlorodiethyl sulphide in the first two stages is substituted in the α-position to give (IV), so this product, although on rare occasions it is chlorinated in the β-position to give (VI), is normally attacked in the α′-position to give ααα′ββ′-*pentachlorodiethyl sulphide* (IX), from which the new tetrachlorinated ethyl vinyl sulphide is derived. It is difficult to predict the course of elimination of hydrogen chloride from (IX), which contains chlorine attached to each carbon atom, but loss of α-chlorine appears more consistent with the facts, and either (X) or (XVII) therefore represents the probable constitution of the second tetrachlorinated ethyl vinyl sulphide; (XVII), however, like the slightly hydrolysable compound (V), contains the chain CHCl:CCl–, and as symmetrical monosubstitution of the other chain could scarcely account for such greatly increased ease of hydrolysis, the new tetrachloro-compound is best formulated as ααβ-*trichloroethyl* β-*chlorovinyl sulphide* (X). This formulation accounts readily for the high hydrolysis and the development of extra acidity, the α-CCl_2 group, on conversion into a carbonyl group, giving rise to a readily hydrolysable unsaturated thioacetic ester.

Assuming this constitution, the derived series (XI), (XII), and (XIII) can be formulated with a fair degree of certainty. The ααα′ββ′β′-*hexachlorodiethyl sulphide* (XI), formed by addition of chlorine to (X), differs from its ααβββ′-isomeride (VIII) in being

somewhat more readily hydrolysed, and in breaking down on refluxing to give an unsaturated pentachloro-sulphide. The latter, which evidently differs in type from (X), for even after 2½ hours' boiling with water it develops less than the theoretical quantity of hydrogen chloride with but a little extra acid, appears to be *αββ-trichloroethyl αβ-dichlorovinyl sulphide* (XII) derived from (XI) by loss of hydrogen chloride from the $-CCl_2{\cdot}CH_2Cl$ chain, the other chain, as found by Lawson and Dawson (*loc. cit.*), being comparatively stable to heat. This, on addition of chlorine, gives *αα′ββ′β′-heptachlorodiethyl sulphide* (XIII), the absence of the grouping $CCl_3{\cdot}CCl_2{\cdot}S$ in which is indicated by the fact that it does not yield hexachloroethane when chlorinated in the cold.

The two unsaturated tetrachloro-compounds, whose very similar boiling points and densities have doubtless led previous observers to assume their identity, are inseparable by fractional distillation, and if, therefore, the two pentachlorodiethyl sulphides (VI) and (IX) should be formed simultaneously during the chlorination of ββ′-dichlorodiethyl sulphide, the derived unsaturated tetrachloro fraction, although distilling as one compound, would be a mixture of the two isomerides and might give any hydrolytic figure between 2% and 70%. As a result of twenty such chlorinations, however, only one instance of low hydrolysis (4·6%) was found, five hydrolysed to the extent of 68—70%, and the remainder gave values between 33% and 66%. The non-production of fractions hydrolysing in the range 5—33% is, we believe, a significant indication that these mixtures do not consist solely of the two isomerides (VII) and (X), but contain in addition a third *tetrachlorinated ethyl vinyl sulphide*, of about 33% hydrolysis, possibly *αβ-dichloroethyl αβ-dichlorovinyl sulphide* (XVII), derived from (IX), the parent of (X), by loss of hydrogen chloride from the other chain. This view appears to derive support from the fact that certain of the fractions of intermediate hydrolysis had a slightly lower boiling point and density than a known mixture of (VII) and (X) of the same hydrolysis, and further, that the higher chlorinated products which they gave did not appear to be identical with the corresponding compounds from (VII) and (X). The third isomeride and its derivatives (XVIII), (XIX), and (XX) have not, however, been isolated in a state of purity.

When ββ′-dichlorodiethyl sulphide is treated with more than 3 mols. of chlorine, any or all of the hexachlorodiethyl sulphides given in the scheme may be produced. In general, the αα′ββ′-tetrachlorodiethyl sulphide (IV) is chlorinated in the α′-position to give (IX), from which the hexachloro-compounds (XI), (XIV), and (XVIII) are obtained by the subsequent entry of chlorine into the β′-, α′-, or β-position, respectively. It is also possible for αα′ββ′

hexachlorodiethyl sulphide (VIII) to be formed, since (IV) can be chlorinated in the β-position, but in the cases examined here, it does not appear to have been produced in any quantity.

In Expt. 35 the hexachlorodiethyl sulphide and the derived pentachlorinated ethyl vinyl sulphide approximated closely in properties to (XI) and (XII) respectively, but in other cases the products were evidently non-homogeneous. In Expt. 36, the hexachloro fraction was not examined, but the derived pentachloro fraction, though distilling as a homogeneous substance, exhibited differences in density in its various sub-fractions; the less dense fractions resembled (XIX) in properties and, like it, furnished a heptachlorodiethyl sulphide which gave hexachloroethane on further chlorination in the cold. The unsaturated tetra- and penta-chloro fractions obtained in this experiment were accompanied by considerable quantities of low-boiling degradation products, presumably formed by the destructive chlorination of one or other of the polychloroethyl sulphides present. As these low-boiling fractions consisted almost exclusively of *as*-tetrachloroethane and *trichloroethyl sulphur chloride* in the approximate molecular ratio 2 : 1, they would appear to be derived from a hexachlorodiethyl sulphide of the constitution (XI) or (XIV), preferably the latter, which could evidently be chlorinated further to give either trichloroethyl sulphur chloride and *as*-tetrachloroethane, or sulphur dichloride and the chlorinated ethane. The excess of the latter would thus be accounted for, since the sulphur dichloride would not have been collected under the conditions of the experiment owing to its higher volatility. The tetrachloroethane could not, in this instance, be produced by the further chlorination of ethylene dichloride (compare Mann and Pope, *loc. cit.*), for the chlorination was carried out at about 20° in the absence of direct sunlight, and, further, neither penta- nor hexa-chloroethane was simultaneously formed.

There would thus appear to be reason for believing that no one hexachlorodiethyl sulphide is exclusively formed by the direct chlorination of ββ'-dichlorodiethyl sulphide, but that the product may be either (XI), (XIV), or (XVIII), or some mixture of these.

In Expt. 17, in which the tri- and tetra-chloro-compounds of Mann and Pope were the chief products, the higher-boiling fractions, on being kept, deposited a small amount of a solid, $C_6H_8Cl_8S_2$, m. p. 70·5°. This, however, is not a simple chlorination product, but is considered to arise during distillation by interaction of some of the chlorinated ethyl vinyl sulphides with the intermediate formation of a sulphonium chloride. Its exact constitution has not been determined, but it appears probable that it is a β-(β-*chloroethyl-thiol*) *ethyl trichlorovinyl sulphide* (XXI) formed by some such scheme

as the following (compare Bell, Bennett, and Hock, J., 1927, 1803) :

$$\begin{matrix}CCl_2{:}CCl\\CH_2Cl{\cdot}CH_2\end{matrix}\!>S + S<\!\begin{matrix}CCl{:}CHCl\\CH_2{\cdot}CH_2Cl\end{matrix} \longrightarrow$$

$$\left[CCl_2{:}CCl{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{Cl}{S}<\!\begin{matrix}CCl{:}CHCl\\CH_2{\cdot}CH_2Cl\end{matrix}\right] \longrightarrow$$

$$CCl_2{:}CCl{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl\ \text{(XXI.)} + CCl_2{:}CHCl$$

On the above hypothesis it is possible for a compound $C_6H_8Cl_4S_2$ *to* be formed in many ways, but in this case the most probable components are those suggested.

EXPERIMENTAL.

I. *Quantitative Chlorination Experiments.*

In experiments 1 to 6 (Table I) a carbon tetrachloride solution of the liquid to be chlorinated was placed in a boiling tube (A), attached to a small reflux condenser. A solution of the requisite amount of chlorine in carbon tetrachloride was placed in an adjoining vessel (B), and the two vessels were so connected that by aspirating dry carbon dioxide-free air through the apparatus the chlorine was slowly transferred *via* a capillary jet into the liquid in the reaction vessel (A). The hydrogen chloride evolved during the chlorination was collected in bubblers containing standard alkali and subsequently estimated by titration. Towards the end of the experiment (B) was gently heated to expel the last traces of chlorine, and the pressure in the apparatus reduced to about 150 mm. to ensure complete removal of hydrogen chloride.

In the second stage of the reaction (B) was removed, and the pressure in the apparatus further reduced, first to 60 mm., to expel the carbon tetrachloride, and subsequently to 15—20 mm., at which pressure the liquid was gently refluxed for some 20 minutes, the hydrogen chloride evolved during the process being collected and estimated as before. The heating was repeated until no further evolution of hydrogen chloride occurred.

Finally, the contents of the reaction vessel were fractionated through a small column. The product was, in general, a mixture of two liquids only, and more or less quantitative separation was therefore possible. Individual products were identified by boiling point and density, the composition of the middle runnings, invariably obtained in small quantity, being approximately estimated from its density.

In the larger-scale experiments (Nos. 7—16, Table I), chlorine was bubbled through the liquid at room temperature until the increase in weight of the latter indicated that the desired stage of chlorination

TABLE I.

Quantitative Chlorination Experiments.

No.	Liquid chlorinated.	Molecular *ratio*, chlorine/liquid.	Quantities (g.-mols.). Liquid.	Chlorine.		HCl evolved *during* chlorination.	HCl *evolved* during heating.	Products of distillation. Unsat. tri-*chloro*-compound.	Unsat. tetra-*chloro*-compound.	Hexa-*chloro*-compound.
	Small-scale experiments:									
1	ββ′-Dichlorodiethyl sulphide	2·24	0·081	0·180		0·187	0·082	0·058	0·018	—
2	,, ,, ...	2·40	0·081	0·195		0·180	0·084	0·045	0·030	—
3	β-Chloroethyl αβ-dichlorovinyl sulphide...	0·29	0·056	0·016		0·0025	0·0145	0·038	0·015	—
4	,, ,, ,, ...	0·47	0·075	0·035		0·007	0·027	0·038	0·032	—
5	β-Chloroethyl αββ-trichlorovinyl sulphide	0·32	0·068	0·022		Negligible	Negligible	—	0·044	0·02
6	,, ,, ,,	0·48	0·055	0·026		,,	,,	—	0·026	0·026
	Large-scale experiments:									
7	ββ′-Dichlorodiethyl sulphide	2·10	2·00	4·20		Continuous	1·75	1·80	Some	—
8	,, ,, ...	2·16	1·18	2·55		,,	1·04	0·90	0·15	—
9	,, ,, ...	2·37	0·77	1·83		,,	0·76	0·45	0·27	—
10	,, ,, ...	3·10	1·00	3·10		,,	0·90	Some	0·85	Some
11	,, ,, ...	3·40	1·20	4·20	not measured	,,	0·65	—	0·55	0·50
12	,, ,, ...	4·10	0·40	1·65		,,	Not measured	—	0·15	0·08 *
13	β-Chloroethyl αβ-dichlorovinyl sulphide...	1·03	0·133	0·14		Slight	0·11	—	0·10	Some
14	,, ,, ,, ...	1·00	0·360	0·36		,,	0·34	—	0·29	—
15	β-Chloroethyl αββ-trichlorovinyl sulphide	0·53	0·340	0·18		Nil	Negligible	—	0·165	0·165
16	,, ,, ,,	1·00	0·200	0·20		,,	,,	—	—	0·180

* Quantities of degradation products.

had been reached. Subsequently the product was gently refluxed under reduced pressure to constant weight, the loss in weight being taken as an approximate measure of the hydrogen chloride evolved during the heating process, and finally the product was fractionated as before.

The results of these quantitative chlorinations are in Table I, in which the quantities of reactants and products of reaction are expressed in gram-molecules.

II. *Examination of the Products of Chlorination.*

The compounds examined, prepared in a manner analogous to that employed in the larger-scale quantitative chlorinations, were purified by repeated fractional distillation through a 60 cm. column under reduced pressure. Densities and viscosities were determined as previously described (J., 1928, 155), and refractive indices with an Abbé refractometer. Rates of hydrolysis, for purposes of comparison, were roughly estimated by refluxing about 0·1 g. of the different substances with 50 c.c. of water for 15 minutes, and for 150 minutes, followed by rapid titration with baryta. The values given below are, in most instances, the mean of at least three such determinations, and are expressed in terms of % Cl split off.

(a) *Chlorination of ββ'-Dichlorodiethyl Sulphide with Two Molecules of Chlorine.*—The unstable ααββ'-tetrachlorodiethyl sulphide (IV) obtained in an impure condition by treating ββ'-dichlorodiethyl sulphide with two molecules of chlorine (Expt. 7), when cleared of dissolved hydrogen chloride by the passage of dry carbon dioxide-free air under reduced pressure, had $d_{4^\circ}^{20^\circ}$ 1·53. On heating to 90—100° even under 2 mm. pressure, it decomposed with evolution of hydrogen chloride and gave β-chloroethyl αβ-dichlorovinyl sulphide (V) in 80—90% yield. The latter, after two fractionations was a colourless mobile liquid, b. p. 107°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·4315, $d_{4^\circ}^{25^\circ}$ 1·4255, η^{20° 0·028 dyne/cm.², and $n_D^{20^\circ}$ 1·5562 (Found: C, 24·8 H, 2·6; Cl, 55·7; *M*, cryoscopic in benzene, 190. Calc. for $C_4H_5Cl_3S$: C, 25·1; H, 2·6; Cl, 55·6%; *M*, 191·5). Hydrolysis 15 minutes, 4; 150 minutes, 12·5% Cl. Oxidation with nitric acid gave β-chloroethanesulphonic acid, identified as the ammonium salt m. p. 198°.

(b) *Chlorination of β-Chloroethyl αβ-Dichlorovinyl Sulphide* (V).—By adding chlorine (1 mol.) to the above unsaturated trichloro compound (Expts. 13, 14), ααβββ'-pentachlorodiethyl sulphide (VI) was obtained as an unstable yellow liquid which, on heating, lost hydrogen chloride and gave β-chloroethyl αββ-trichlorovinyl sulphide (VII) in 70—80% yield. The latter, after three fractionations, had b. p. 122—124°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·5425, $d_{4^\circ}^{25^\circ}$ 1·5361, η^{20° 0·039 dyne/cm.

and $n_D^{20°}$ 1·5700 (Found: C, 21·4; H, 1·9; Cl, 62·8; *M*, cryoscopic in benzene, 225. Calc. for $C_4H_4Cl_4S$: C, 21·25; H, 1·8; Cl, 62·8%; *M*, 226). Hydrolysis: 15 minutes, 2; 150 minutes, 10% Cl. On oxidation with nitric acid it gave β-chloroethanesulphonic acid. The lower density given previously (*loc. cit.*) was that of a sample of the tetrachloro-compound obtained directly from ββ′-dichlorodiethyl sulphide [compare (d) below].

(c) *Chlorination of* β-*Chloroethyl* αββ-*Trichlorovinyl Sulphide* (VII).—From the above unsaturated tetrachloro-compound, by addition of one molecule of chlorine (Expt. 16), ααβββ′-hexachlorodiethyl *sulphide* (VIII) *was obtained in* 90% *yield as a stable viscid fluid* which, after purification, had b. p. 158—159°/15 mm., $d_{4°}^{20°}$ 1·6849, $d_{4°}^{25°}$ 1·6794, $\eta^{20°}$ 0·254 dyne/cm.^{2}, and $n_D^{20°}$ 1·5683 (Found: C, 16·25; H, 1·4; Cl, 71·7; *M*, cryoscopic in benzene, 297. Calc. for $C_4H_4Cl_6S$: C, 16·2; H, 1·4; Cl, 71·7%; *M*, 297). Hydrolysis: 15 minutes, 14; 150 minutes, 33% Cl. On further chlorination, even in the cold, hexachloroethane, m. p. 186—187°, was obtained. When the hexachloro-sulphide was heated at 200°/100—120 mm. for 4 hours, an unstable yellow oil slowly distilled, in too small quantity, however, for identification. The residue, on fractionation, yielded 40% of unchanged hexachlorodietbyl sulphide, but no definite lower-boiling fraction could be isolated.

(d) *Chlorination of* ββ′-*Dichlorodiethyl Sulphide with Three Molecules of Chlorine.*—When ββ′-dichlorodiethyl sulphide was treated *with three molecules of chlorine (Expt. 10), the pentachlorodiethyl sulphide* obtained (Found: Cl, 66·5. $C_4H_5Cl_5S$ requires Cl, 67·6%), when freed from dissolved hydrogen chloride, had $d_{4°}^{20°}$ 1·57. Like that described in (b), however, it lost hydrogen chloride on heating to give an unsaturated tetrachloro-compound in 75% yield.

An unsaturated tetrachloro fraction was always obtained when ββ′-dichlorodiethyl sulphide was chlorinated with more than two molecules of chlorine, and the product subsequently decomposed by heating, but out of twenty such chlorinations (Table II), in one case only (Expt. 17) did this fraction appear to be identical with the β-chloroethyl αββ-trichlorovinyl sulphide described in (b) above. In this one instance, 3·86 mols. of the sulphide were treated with about 8·88 mols. of chlorine in diffused daylight, and the β-chloroethyl αβ-dichlorovinyl sulphide (2·3 mols.), b. p. 79·2°/3 mm., obtained on fractionation was accompanied by an unsaturated tetrachloro-sulphide (0·8 mol.), b. p. 87·5—88·5°/2·6 mm., having $d_{4°}^{20°}$ 1·542, and a 15-minute hydrolysis of 4·5% Cl (Found: C, 21·2; H, 1·8; Cl, 62·5%). This was slightly impure β-chloroethyl αββ-trichlorovinyl sulphide. The higher-boiling fractions (b. p. 157—167°/2·5—3 mm.) obtained in this experiment deposited, on standing, a white solid,

TABLE II.

Formation of Unsaturated Tetrachloro-sulphides by the Chlorination of ββ′-Dichlorodiethyl Sulphide.

Expt. No.	Molecular ratio, chlorine/*ββ′*-dichloro-diethyl sulphide.	Rate of increase of wt. during *chlorination* (g. per min.).	Pressure *during* decomposition (mm.).	15-Min.-hydrolysis of unsat. tetrachloro fraction obtained.	Other products obtained.
17	2·30	—	—	4	Unsaturated trichloro-compound
18	2·41	0·74	30	33	
19	2·46	1·00	40—50	39	
20	2·85	0·48	40—50	43	
21	3·00	1·00	80	68	None
22	3·00	1·00	40—50	49	
23	3·00	1·00	30—40	33	
24	3·00	1·00	30—40	34	
25	3·00	0·62	30	50	
26	3·02	1·00	30	39	
27	3·02	1·00	30	38	
28	3·02	1·50	30	53	
29	3·03	0·05	120	69	
30	3·04	0·80	100	69	
31	3·06	1·60	20	54	
32	3·06	1·60	80—90	59	
33	3·30	0·60	80	65	Hexachloro-compounds
34	3·60	0·70	50—60	56	
35	4·08	0·30	80	70	Hexachloro-compounds and degradation products
36	4·12	—	—	69	

crystallising from alcohol in long flat needles, m. p. 70·5°, apparently a β-(β-*chloroethyl-thiol*)*ethyl trichlorovinyl sulphide* (XXI) (Found: C, 25·2; H, 2·8; Cl, 49·6; S, 22·3; *M*, cryoscopic in benzene, 271—286. $C_6H_8Cl_4S_2$ requires C, 25·2; H, 2·8; Cl, 49·6; S, 22·4%; *M*, 286).

On five other occasions (Expts. 21, 29, 30, 35, and 36) when ββ′-dichlorodiethyl sulphide was treated with 3—4 molecules of chlorine, the unsaturated tetrachloro fraction obtained on distillation appeared to be *ααβ-trichloroethyl β-chlorovinyl sulphide* (X). This, after three fractionations, was a colourless mobile liquid, b. p. 122—123°/15 mm., $d^{20^\circ}_{4^\circ}$ 1·5404, $d^{25^\circ}_{4^\circ}$ 1·5342, η^{25° 0·057 dyne/cm.², and $n_D^{20^\circ}$ 1·5661 (Found: C, 21·3; H, 1·9; Cl, 63·0; *M*, cryoscopic in benzene, 227. $C_4H_4Cl_4S$ requires C, 21·25; H, 1·8; Cl, 62·8%; *M*, 226). When it was boiled with water for 15 minutes, or for 150 minutes, acid equivalent to 70% Cl was liberated, but of this, 58—59% only was found by Volhard estimation to be due to hydrochloric acid.

By reason of their identical boiling points, the two isomeric unsaturated tetrachloro-sulphides, when admixed, could not be separated by fractionation, all portions of the distillate being hydro-

lytically and otherwise identical. The density and other physical properties of such mixtures are approximately linear functions of the composition, a known mixture of the two in about equal proportion (actually 53% of VII to 47% of X) having $d_{4^\circ}^{25^\circ}$ 1·5346, η^{20° 0·047 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5679, as compared with values calculated on an additive basis of 1·5352, 0·047, and 1·5681, respectively. By careful fractionation of this mixture, first and last fractions were obtained having 15-minute hydrolyses of 31 and 34% Cl, respectively, that of the original mixture being 33% Cl (Calc.: on an additive basis, 33% Cl).

In the other fourteen cases examined (see Table II), some of the unsaturated tetrachloro fractions obtained, all of which had 15-minute hydrolyses between 33 and 65% Cl, differed slightly in properties from such known mixtures, and appeared to contain a third isomeride, possibly *αβ-dichloroethyl αβ-dichlorovinyl sulphide* (XVII), having a 15-minute hydrolysis of about 33% Cl. The latter apparently formed the chief constituent of the unsaturated tetrachloro fractions obtained in Expts. 18, 23, and 24, these, after repeated fractionation, yielding a colourless liquid, b. p. 120—121°/15 mm., $d_{4^\circ}^{15^\circ}$ 1·544 (Mann and Pope, *loc. cit.*, give $d_{4^\circ}^{15^\circ}$ 1·5441 for their so-called αββ′-tetrachlorodiethyl sulphide), $d_{4^\circ}^{20^\circ}$ 1·5378, $d_{4^\circ}^{25^\circ}$ 1·5315, η^{20° 0·046 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5673 (Found: C, 21·4; H, 1·9; Cl, 62·7. $C_4H_4Cl_4S$ requires C, 21·25; H, 1·8; Cl, 62·8%). Hydrolysis: 15 minutes, 33% Cl. The boiling point and density of this substance are, it will be observed, slightly but definitely lower than those of either of the other two isomerides.

Some of these unsaturated tetrachloro fractions of intermediate hydrolysis yielded hexachloroethane on chlorination beyond the hexachloro-stage, indicating the presence in them of β-chloroethyl αββ-trichlorovinyl sulphide [compare (c) above], but the amount appeared to be relatively small.

The rate at which the chlorination of ββ′-dichlorodiethyl sulphide was carried out did not, apparently, influence the course of the reaction to any great extent, but from the data in Table II it would appear that production of unsaturated tetrachloro fractions having intermediate hydrolysis was favoured by the employment of comparatively low pressures during the preliminary decomposition process, fractions rich in ααβ-trichloroethyl β-chlorovinyl sulphide, and hence having high hydrolysis, being, in general, obtained when pressures of 80—120 mm. were used.

(e) *Chlorination of ααβ-Trichloroethyl β-Chlorovinyl Sulphide* (X).—When ααβ-trichloroethyl β-chlorovinyl sulphide was treated with chlorine (1 mol.) in the cold, slight evolution of hydrogen chloride occurred, but the main reaction was one of addition, ααα′ββ′β′-hexa-

chlorodiethyl sulphide (XI) being obtained in 70—75% *yield.* This, after two fractionations, was a colourless oily liquid, b. p. 159—160°/15 mm., $d_4^{20°}$ 1·6841, $d_4^{25°}$ 1·6783, $\eta^{20°}$ 0·294 dyne/cm.^{2}, and $n_D^{20°}$ 1·5681 (Found: C, 16·2; H, 1·3; Cl, 71·7; *M*, cryoscopic in benzene, 296. $C_4H_4Cl_6S$ requires C, 16·2; H, 1·4; Cl, 71·7%; *M*, 297). Hydrolysis: 15 minutes, 31; 150 minutes, 55% Cl.

On heating at 200°/100—120 mm. for 3—4 hours, this hexachloro-sulphide, unlike its ααβββ′-isomeride [compare (c) above], lost hydrogen chloride and gave an unsaturated pentachloro-derivative, αββ-*trichloroethyl* αβ-*dichlorovinyl sulphide* (XII), in 65—70% yield. The latter after three fractionations was a colourless liquid, b. p. 134—135°/15 mm., $d_4^{20°}$ 1·6293, $d_4^{25°}$ 1·6236, $\eta^{20°}$ 0·065 dyne/cm.^{2}, and $n_D^{20°}$ 1·5778 (Found: C, 18·5; H, 1·35; Cl, 68·2; *M*, cryoscopic in benzene, 260. $C_4H_3Cl_5S$ requires C, 18·4; H, 1·2; Cl, 68·1%; *M*, 260). Hydrolysis: 15 minutes, 32·5; 150 minutes, 66% Cl; of the latter, however, only 59% was found by Volhard estimation to be due to hydrochloric acid.

By the addition of one molecule of chlorine in the cold to this unsaturated pentachloro-compound, and fractionation of the product, αα′βββ′β′-*heptachlorodiethyl sulphide* (XIII) was obtained in 60—70% yield as a colourless viscid liquid, b. p. 170—172°/15 mm., $d_4^{20°}$ 1·7473, $d_4^{25°}$ 1·7415, $\eta^{20°}$ 0·427 dyne/cm.^{2}, and $n_D^{20°}$ 1·5741 (Found: C, 14·5; H, 0·9; Cl, 74·8; *M*, cryoscopic in benzene, 329. $C_4H_3Cl_7S$ requires C, 14·5; H, 0·9; Cl, 74·9%; *M*, 331). Hydrolysis: 15 minutes, 4; 150 minutes, 32% Cl. No hexachloroethane was obtained when this heptachloro-sulphide was further chlorinated in the cold.

All the above compounds, and also the unsaturated tetrachloro-sulphide from which they were derived, appeared to evolve hydrogen sulphide during hydrolysis.

(f) *Chlorination of Unsaturated Tetrachloro Fractions of Intermediate Hydrolysis.*—By the addition of one molecule of chlorine to unsaturated tetrachloro fractions of intermediate hydrolysis [see (d) above], and repeated fractionation of the product, a saturated hexachloro-sulphide, presumably mainly αα′βββ′-*hexachlorodiethyl sulphide* (XVIII), was obtained in 70% yield; b. p. 157—159°/15 mm., $d_4^{20°}$ 1·6825, $d_4^{25°}$ 1·6763, $\eta^{20°}$ 0·273 dyne/cm.^{2}, and $n_D^{20°}$ 1·5681 (Found: C, 16·5; H, 1·3; Cl, 71·6. $C_4H_4Cl_6S$ requires C, 16·2; H, 1·4; Cl, 71·7%). Hydrolysis: 15 minutes, 25; 150 minutes, 56% Cl.

This, when heated at 200°/100—110 mm. for 3 hours, lost hydrogen chloride to form an unsaturated pentachloro-sulphide, possibly αβ-*dichloroethyl* αββ-*trichlorovinyl sulphide* (XIX), in 60% yield, which, after three fractionations, had b. p. 133—134°/15 mm.,

$d_4^{20^\circ}$ 1·6190, $d_4^{25^\circ}$ 1·6131, η^{20° 0·063 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5770 (Found: C, 18·3; H, 1·4; Cl, 67·6. $C_4H_3Cl_5S$ requires C, 18·4; H, 1·2; Cl, 68·1%). Hydrolysis: 15 minutes, 32; 150 minutes, 66% Cl. Of the latter, 60% was found by Volhard estimation to be due to hydrochloric acid.

When this unsaturated pentachloro-sulphide was treated with chlorine (1 mol.) in the cold, hydrogen chloride was evolved continuously, but only the addition product could be separated on fractionation (yield, 50%). This, apparently *αα*α'ββββ'-*heptachlorodiethyl sulphide* (XX), was obtained in too small quantity to permit of adequate purification, but after one further fractionation through a small column, it had b. p. 132—134°/*ca.* 2 mm., $d_4^{20^\circ}$ 1·743, $d_4^{25^\circ}$ 1·737, η^{20° 0·382 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5741 (Found: C, 14·4; H, 1·0; Cl, 74·5. $C_4H_3Cl_7S$ requires C, 14·5; H, 0·9; Cl, 74·9%). Hydrolysis: 15 minutes, 8% Cl. On further chlorination in the cold hexachloroethane was obtained.

All these compounds, like those described in (*d*) and (*e*) above, evolved during hydrolysis a vapour having an odour like that of hydrogen sulphide.

(*g*) *Chlorination of* ββ'-*Dichlorodiethyl Sulphide with Four Molecules of Chlorine.*—The complete conversion of ββ'-dichlorodiethyl sulphide into hexachloro-sulphides by treatment with chlorine (4 mols.) in the cold was not found possible, maximum yields being obtained when about 3·5 mols. of chlorine were used (compare Expt. 11). Chlorination beyond this point resulted in partial destruction of the hexachloro-sulphides already formed, low-boiling chlorinated hydrocarbons and other degradation products being obtained on subsequent distillation, together with a residual tetrachloro fraction (compare Expts. 12, 35, and 36).

By reason of the number of isomerides possible and of the extreme difficulty of separating them, no attempt was made to isolate and identify the hexachlorodiethyl sulphides obtained in these experiments, investigation of the products of the reaction being restricted to an examination of the accompanying degradation products, and of the unsaturated pentachloro-compounds resulting from the decomposition of the hexachloro fractions.

In Expt. 35, the hexachloro-sulphide obtained (Found: C, 16·1; H, 1·5; Cl, 71·6%) had b. p. 158—159°/15 mm., $d_4^{20^\circ}$ 1·6787, and η^{20° 0·284 dyne/cm.^{2}, and decomposed, on being heated at 200°/100 mm. for 4 hours, to give an unsaturated pentachloro-sulphide having b. p. 133—134°/15 mm., $d_4^{20^\circ}$ 1·6237, η^{20° 0·067 dyne/cm.^{2}, $n_D^{20^\circ}$ 1·5783, and 15-minute hydrolysis of 33% Cl (Found: C, 18·3; H, 1·3; Cl, 67·8%). These values approximate closely to those found for αα'ββ'β'-hexachlorodiethyl sulphide (XI) and its decomposition

product, αββ-trichloroethyl αβ-dichlorovinyl sulphide (XII), respectively [compare (e) above].

In Expt. 36, in which 5·37 mols. of ββ'-dichlorodiethyl sulphide were treated with 22·12 mols. of chlorine, the product, after decomposition by heating and subsequent fractionation, yielded 0·6 mol. of αααβ-tetrachloroethane, b. p. 35—36°/20 mm. or 129—129·7°/760 mm. (Found: C, 14·7; H, 1·2; Cl, 84·5. Calc. for $C_2H_2Cl_4$: C, 14·3; H, 1·2; Cl, 84·5%), together with 0·26 mol. of an unstable yellow liquid, b. p. 53·8°/3·5 mm., which appeared to be impure *trichloroethyl sulphur chloride* (Found: C, 13·4; H, 1·1; Cl, 69·1; S, 15·0; *M*, cryoscopic in benzene, 191. $C_2H_2Cl_4S$ requires C, 12·0; H, 1·0; Cl, 71·0; S, 16·0%; *M*, 200).

Owing to the comparatively high pressure employed, the hexachlorodiethyl sulphide formed in this experiment underwent more or less complete decomposition during the preliminary heating process. The unsaturated pentachloro-sulphide derived from it, and occurring in the distillate, appeared to consist chiefly of αβ-dichloroethyl αββ-trichlorovinyl sulphide (XIX), the middle portion, after purification, having b. p. 133·5—134°/15 mm., $d_{4°}^{20°}$ 1·6183, $d_{4°}^{25°}$ 1·6125, $\eta^{20°}$ 0·069 dyne/cm.², and $n_D^{20°}$ 1·5750 (Found: C, 18·55; H, 1·15; Cl, 67·7. $C_4H_3Cl_5S$ requires C, 18·4; H, 1·2; Cl, 68·1%). Hydrolysis: 15 minutes, 31; 150 minutes, 66% Cl; 63% of the latter being actually due to hydrochloric acid. When this portion was treated with one molecule of chlorine, absorption took place, accompanied by evolution of hydrogen chloride, and the product, on fractionation, yielded a *heptachlorodiethyl sulphide*, b. p. 144—146°/5·5 mm., $d_{4°}^{20°}$ 1·7373, $d_{4°}^{25°}$ 1·7325, $\eta^{20°}$ 0·379 dyne/cm.², $n_D^{20°}$ 1·5739 (Found: C, 14·4; H, 1·0; Cl, 74·8. $C_4H_3Cl_7S$ requires C, 14·5; H, 0·9; Cl, 74·9%), and hydrolysis: 15 minutes, 5; 150 minutes, 30% Cl, which yielded hexachloroethane on further chlorination.

The higher-boiling portion of the pentachloro fraction obtained in this experiment appeared to contain a heavier isomeride, possibly (XII) or (XV) or both. It had b. p. 134—134·5°/15 mm., $d_{4°}^{20°}$ 1·6248, $d_{4°}^{25°}$ 1·6195, and $\eta^{20°}$ 0·069 dyne/cm.² (Found: C, 18·4; H, 1·2; Cl, 67·5; S, 12·4. $C_4H_3Cl_5S$ requires C, 18·4; H, 1·2; Cl, 68·1; S, 12·3%). Hydrolysis, 15 minutes, 36% Cl. Both fractions evolved a vapour resembling hydrogen sulphide during hydrolysis.

In none of the cases examined was ααββββ'-hexachlorodiethyl sulphide (VIII) formed in appreciable quantity by the treatment of ββ'-dichlorodiethyl sulphide with four molecules of chlorine, hexachloroethane being absent from the degradation products. as-Tetrachloroethane and yellow oils resembling trichloroethylsulphur chloride were of frequent occurrence in the latter, and the accompanying

unsaturated tetrachloro fractions consisted for the most part of ααβ-trichloroethyl β-chlorovinyl sulphide (X).

Summary.

An extended study of the chlorination of ββ′-dichlorodiethyl sulphide with two and more mols. of chlorine has confirmed the view, advanced previously (J., 1928, 155) and independently of the work of Lawson and Dawson (*J. Amer. Chem. Soc.*, 1927, **49**, 3119, 3125), that the αββ′-trichloro- and αββ′β′-tetrachloro-diethyl sulphides of Mann and Pope (J., 1922, **131**, 594) are β-chloroethyl αβ-dichlorovinyl and αββ-trichlorovinyl sulphides, respectively, and that the formation of chloroethyl chlorovinyl sulphides is in all cases due to the loss of hydrogen chloride from saturated polychlorodiethyl sulphides, which are the first, but less stable products of chlorination. Further, contrary to previous views, chlorination is not confined to one chain, as is proved by the isolation from amongst the products of direct chlorination of ββ′-dichlorodiethyl sulphide of new tetra- and penta-chlorinated ethyl vinyl sulphides and hexachlorodiethyl sulphides. The pentachlorinated ethyl vinyl sulphides furnish heptachlorodiethyl sulphides on further addition of chlorine. A mechanism of the course of chlorination is suggested.

EXPERIMENTAL STATION, PORTON, SALISBURY.

RESEARCH ESTABLISHMENT, SUTTON OAK, ST. HELENS, LANCS.

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LXXX.—*The Nitration of Benzylpyridines and the Oxidation of Benzylpiperidines.*

By FRANK BRYANS and FRANK LEE PYMAN.

THE nitration of the 2-, 3-, and 4-benzylpyridines was undertaken as a sequel to the nitration of the 2-, 3-, and 4-phenylpyridines (Forsyth and Pyman, J., 1926, 2912), and it was found that the proportion of the meta-isomeride produced (in the case of the 2- and 4-substituted compounds) was greatly diminished in the benzylpyridines as compared with the phenylpyridines, the yields of the nitro-compounds (or oriented degradation products) being as follows :—

Yields (%) of Nitration Products.

	Phenylpyridines.			Benzylpyridines.		
	2-.	3-.	4-.	2-.	3-.	4-.
o	5·1	—	12·7	—	—	—
m	34·9	—	28·5	10·4	—	4·8
p	42·3	64·3	38·0	66·7	63·1	70·2

These results harmonise with Goss, Hanhart, and Ingold's observations (J., 1927, 250) that β-phenylethylamines yield a much smaller proportion of the *m*-nitro-substituted compounds (12% in the case of β-phenylethylamine) than do the benzylamines (49% in the case of benzylamine).

Since we were in possession of quantities of the 2- and 4-benzylpyridines, it appeared to us to be of interest to determine whether their reduction products, the 2- and 4-benzylpiperidines, and also *2-benzyl-1-methylpiperidine*, underwent the same type of fission on oxidation with sulphuric acid and manganese dioxide as the 1-benzyltetrahydro*iso*quinolines or 1-benzyl-2-methyltetrahydro*iso*quinolines (Pyman, J., 1909, **95**, 1266, 1738). This, however, proved not to be the case.

EXPERIMENTAL.

The 2- and 4-benzylpyridines were prepared by the action of benzyl chloride on pyridine, and separated either by fractionation of the picrates (Tschitschibabin's method, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 249; 1915, **47**, 1297) or by fractional distillation under atmospheric pressure. These bases, their reduction products, the 2- and 4-benzylpiperidines, and the picrates of each had the b. p.'s or m. p.'s recorded by Tschitschibabin. The following new derivatives were prepared:

1-*Benzenesulphonyl-2-benzylpiperidine*, prisms from ligroin, m. p. 65° (corr.) (Found: C, 68·2; H, 6·9; S, 9·8. $C_{18}H_{21}O_2NS$ requires C, 68·6; H, 6·7; S, 10·2%).

1-*Benzoyl-2-benzylpiperidine*, microscopic needles from ligroin m. p. 68° (corr.) (Found: C, 81·5; H, 7·7; N, 4·8. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·5; N, 5·0%).

1-*Benzenesulphonyl-4-benzylpiperidine*, needles from alcohol, m. p 118° (corr.) (Found: C, 68·6; H, 6·7; S, 9·9. $C_{18}H_{21}O_2NS$ require C, 68·6; H, 6·7; S, 10·2%).

2-Benzyl-1-methylpiperidine could not be prepared by th reduction of 2-benzylpyridine metho-salts, but was obtained in poo yield (12%) by heating 2-benzylpiperidine (6 g.) with methy iodide (5 g.) for 10 hours at 130°, 2-benzylpiperidine being remove from the tertiary bases obtained as the benzoyl derivative. Th *picrate* crystallised from alcohol in yellow prisms, m. p. 181° (corr (Found: N, 13·1. $C_{19}H_{22}O_7N_4$ requires N, 13·4%). The bas regenerated from the picrate had b. p. 305—310°/740 mm.

Nitration of 2-Benzylpyridine.—*2-Benzylpyridine nitrate* [anhyd ous prisms from dilute nitric acid, m. p. 116° (corr.) (Found: C, 61·7; H, 5·2. $C_{12}H_{11}N,HNO_3$ requires C, 62·1; H, 5·2%)] (10 g was added to concentrated sulphuric acid (20 c.c.), cooled in ic

during ½ hour. The mixture was warmed at 50° for 5 minutes, poured on ice, and precipitated fractionally by ammonia, giving first 2-*p*-nitrobenzylpyridine (5·42 g.; m. p. 76—78°), then an oil (3·72 g.). Attempts to separate this oil by fractional precipitation of the base from a salt, or by fractional crystallisation of various salts, were unsuccessful, but on oxidation in neutral suspension with potassium permanganate (5 g.) in water (400 c.c.), it gave a mixture of nitrobenzoylpyridines (3·3 g., m. p. 85—100°). When this was treated with a limited quantity of water, 2-*m*-nitrobenzoylpyridine (1·05 g.; m. p. 117—120°) remained undissolved; the solution deposited 2-*p*-nitrobenzoylpyridine (0·8 g.; m. p. 105°). The yields of nitration products isolated are thus para 66·7, and meta 10·4% of the theoretical.

2-*p*-Nitrobenzylpyridine had m. p. 81° (T.,* 81°); its picrate, m. p. 185—187° (T., 185°); nitrate, m. p. 132° (corr.); and hydrochloride, m. p. 190° (corr.). It gave on oxidation 2-*p*-nitrobenzoylpyridine, m. p. 105° (T., 103°), giving a hydrochloride, m. p. 187° (Koenigs, *Ber.*, 1926, **59**, 1717, gives m. p. 173°).

2-m-*Nitrobenzoylpyridine* crystallises from alcohol in prisms or from water in needles, m. p. 122° (corr.) (Found: C, 63·0; H, 3·5. $C_{12}H_8O_3N_2$ requires C, 63·2; H, 3·5%). Its orientation was determined by oxidation with permanganate, *m*-nitrobenzoic acid (m. p. 140° alone or mixed with a known specimen) being isolated in 14% yield.

Nitration of 3-Benzylpyridine.—3-*Benzylpyridine nitrate* [anhydrous prisms from dilute nitric acid, m. p. 140° (corr.) (Found: C, 61·8; H, 5·0%)] (3 g.) was added slowly to concentrated sulphuric acid (10 c.c.) cooled in ice. The mixture was warmed at 50° for 5 minutes, poured on ice, and fractionally precipitated with ammonia. The first two crops (1·52 g.) became crystalline and after recrystallisation from alcohol gave pure 3-*p*-nitrobenzylpyridine (1·44 g.; m. p. 88°). Later crops (1·30 g.) were oily and were converted into nitrate; when this was crystallised from a large volume of aqueous alcohol, the nitrate of the *p*-isomeride separated (0·14 g., m. p. 157°). Previous attempts to effect the further separation of similar mixtures of nitro-3-benzylpyridines either as such or as the nitrobenzoylpyridines having proved fruitless, on this occasion the mixture was oxidised with permanganate; a mixture of nitrobenzoic acids (0·23 g.) was then obtained from which 0·09 g. of *p*-nitrobenzoic acid (m. p. 234°) and a trace of *m*-nitrobenzoic acid (m. p. 118—125°) were isolated.

The yields of nitration products are thus para, 63·1%; meta, trace.

* T = Tschitschibabin.

3-p-*Nitrobenzylpyridine* crystallises from alcohol in small colourless prisms, m. p. 88° (corr.) (Found: C, 67·5; H, 4·8. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7%). It is sparingly soluble in water, but readily soluble in alcohol or ether. The *picrate* crystallises from alcohol as a flocculent mass of needles, m. p. 145—146° (corr.) (Found: N, 15·4. $C_{12}H_{10}O_2N_2,C_6H_3O_7N_3$ requires N, 15·8%). The nitrate forms clusters of needles, m. p. 157° (corr.), from water or alcohol.

3-p-*Nitrobenzoylpyridine* was prepared by heating the above base (1·4 g.) with potassium permanganate (7 g.) in 3% aqueous solution for ½ hour, destroying the excess of permanganate with alcohol, and filtering the solution; it separated, on cooling, in needles, m. p. 106° (corr.), the yield being 1·0 g. (Found: C, 62·9; H, 3·6. $C_{12}H_8O_3N_2$ requires C, 63·2; H, 3·5%). Its picrate crystallised from alcohol in glistening plates, m. p. 185—187° (corr.). The final mother-liquor from the permanganate oxidation was acidified and gave *p*-nitrobenzoic acid (0·21 g., m. p. 235°; mixed m. p. 235°), whence the orientation of the nitro-group in the above bases is known.

Nitration of 4-*Benzylpyridine.*—4-*Benzylpyridine nitrate* [anhydrous prisms, m. p. 110° (corr.), from dilute nitric acid (Found: C, 62·3; H, 5·1%)] (16 g.) was added to concentrated sulphuric acid (30 c.c.), cooled with ice, in the course of ½ hour. The mixture was warmed at 50° for 5 minutes, poured on ice, basified with ammonia, and extracted with ether. The extract gave an oil (15·6 g.) which crystallised on keeping, and after recrystallisation from alcohol gave 4-*p*-nitrobenzylpyridine (9·9 g., m. p. 74°). The alcoholic mother-liquor left an oil, which was oxidised with permanganate and gave a mixture of nitro-4-benzoylpyridines (3·1 g., m. p. 80—100°). This material was converted into hydrochlorides and crystallised fractionally from alcohol, giving first 4-*m*-nitrobenzoylpyridine hydrochloride (0·87 g., m. p. 245°; giving with ammonia the base, m. p. 129°), then the hydrochloride (0·9 g., m. p. 198°) of the para-isomeride, which gave with ammonia pure 4-*p*-nitrobenzoylpyridine (0·5 g., m. p. 121°). The final liquor was concentrated and basified, and the precipitate crystallised to constant m. p. from water; a substance (0·34 g.) of m. p. 75° was then obtained which is presumably 4-*o*-nitrobenzoylpyridine. The yields of nitration products isolated are thus para 70·2, meta 4·8%.

4-*p*-Nitrobenzylpyridine had m. p. 74° (T., 74°); its picrate m. p. 168° (T., 167°). 4-*p*-Nitrobenzoylpyridine had m. p. 121° (T., 123°).

4-m-*Nitrobenzoylpyridine* crystallises from water in needles m. p. 129° (corr.) (Found: C, 62·8; H, 3·9. $C_{12}H_8O_3N_2$ require C, 63·2; H, 3·5%). On oxidation with potassium permanganat

it gave *m*-nitrobenzoic acid (m. p. 140°; mixed m. p. 140°) in 25% yield.

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MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, February 15th*, 1929.]

LXXXI.—*The Rearrangement of Phenyl Benzyl Ethers.*

By WALLACE FRANK SHORT and MARTIN LOUIS STEWART.

THE rearrangement of phenyl benzyl ether has been observed by van Alphen (*Rec. trav. chim.*, 1927, **46**, 804) and by Short (J., 1928, 528). The former obtained a small quantity of 4-hydroxydiphenylmethane by heating phenyl benzyl ether to 160° with 40% of anhydrous zinc chloride. Short heated phenyl benzyl ether with the catalyst until a visible reaction set in (225° with zinc chloride * alone, 180° with zinc chloride and a current of hydrogen chloride) and isolated phenol and 2- and 4-hydroxydiphenylmethane. Van Alphen holds that the reaction is intramolecular, but in view of the experimental results set out below we consider that the reaction, like the rearrangement of alkylaniline hydrochlorides (Beckmann and Correns, *Ber.*, 1922, **55**, 852; compare, however, Derrick, *J. Amer. Chem. Soc.*, 1924, **46**, 166; Hickinbottom, J., 1927, 64) and of the diacylanilines (Chapman, J., 1925, **127**, 2818), is intermolecular.

(i) 2:4-Dibenzylphenol is one of the main products of the rearrangement of phenyl benzyl ether under all the conditions tried.

(ii) Phenyl benzyl ether is attacked by hydrogen chloride at 100° with the formation of benzyl chloride and phenol, which are known to react to form 2- and 4-hydroxydiphenylmethane. Table I shows the products obtained from 100 g. of phenyl benzyl ether.

The necessity for a catalyst and the absence of dibenzyl in the products show that the benzyl does not migrate as a free radical.

(iii) When the rearrangement of phenyl benzyl ether is carried out in presence of anisole (1 mol.), more than half the benzyl becomes attached to the anisole nucleus (B, Table II). Appropriation by the anisole is probably favoured by the smaller initial concentration of the phenol, and competition experiments (A, Table II) in which benzyl chloride was heated with equivalent quantities of phenol and anisole bear this out.

* It is well known that zinc chloride, if it is at all damp, may contain free hydrogen chloride.

TABLE I.

	A.	B.	C.
Temperature	*160°*	*100°*	*100°*
Catalyst	$ZnCl_2$(40 g.)	$ZnCl_2$(2 g.); HCl	HCl
Duration (hours)	1	3	3
Phenol	23·8	13·4	25·0
Benzyl chloride	—	—	9·0
2-Hydroxydiphenylmethane	9·0	—	7·6
4-Hydroxydiphenylmethane	19·4	28·4	12·6
2 : 4-Dibenzylphenol	40·4	15·0	12·6
Resinous material	27·4 *	36·6	33·2 *

* By difference.

TABLE II.

Products (g.) from 0·4 g.-mol. quantities.	A. Condensation.	B. Rearrangement.
Hydroxydiphenylmethanes	17·0	14·0
2 : 4-Dibenzylphenol	6·6	12·6
4-Methoxydiphenylmethane	21·7	28·5
2 : 4-Dibenzylanisole	1·9	3·4
Partition of benzyl chloride, PhOMe/PhOH	1·07	1·35

Condensation of quinol monomethyl ether with benzyl chloride gives a homogeneous product in which the benzyl is doubtless directed ortho by the hydroxyl. This is another illustration of the fact first established by Wibaut (*Rec. trav. chim.*, 1915, **34**, 241) that the velocity of substitution induced by the simultaneous presence of two substituents in the benzene nucleus may be wholly different from that induced by the substituents separately.

The identification of 2- and 4-hydroxydiphenylmethane was confirmed in all cases by the preparation of their *benzyl* ethers, which we have synthesised. A very small capacity for crystallisation appears to be characteristic of the dibenzylphenols and their derivatives. 2 : 4- and 2 : 6-*Dibenzylphenol*, which are strongly cryptophenolic, were prepared from benzyl chloride and the sodium derivative of 4- and 2-hydroxydiphenylmethane, respectively, in dry toluene. Claisen has shown (*Annalen*, 1925, **442**, 238) that phenols are benzylated in the *ortho*-position by this method, and potash fusion of the isomeride believed to be 2 : 4-dibenzylphenol now gives a small yield of 4-hydroxy*iso*phthalic acid, which helps to confirm this. 2 : 4-Dibenzylphenol was identified in all cases by the preparation of its *α-naphthylurethane*.

EXPERIMENTAL.

Phenyl benzyl ether was obtained in 73% yield by a modification of the method due to Gomberg and Buchler (*J. Amer. Chem. Soc.*, 1920, **42**, 2066). A solution of phenol (140 g.; 1·5 mols.) in 600 c.c. of aqueous sodium hydroxide (60 g.; 1·5 mols.) was boiled gently for 1 hour with benzyl chloride (126 g.; 1 mol.). Unchanged

phenol was removed from an ethereal solution of the product by extraction with alkali. The solvent was removed from the dried solution, and the residue yielded pure phenyl benzyl ether (m. p. 39°) on recrystallisation from 95% alcohol.

2-Hydroxydiphenylmethane and 2 : 6-*Dibenzylphenol*.—Sodium phenoxide (from 94 g. of phenol) was condensed with benzyl chloride (126 g.) in dry toluene as described by Claisen (*Annalen*, 1925, **442**, 238). Phenol and 2-hydroxydiphenylmethane (m. p. 21°) were extracted from the product by means of alkali. The residue from the toluene solution was repeatedly fractionated at 10 mm. and yielded two main fractions: (1) 150—153°, (2) 237·5—238°. The first fraction solidified completely and after recrystallisation from alcohol melted at 38—39° and did not depress the m. p. of phenyl benzyl ether. The production of this ether is probably due to the presence of phenol, produced in the reaction $2PhONa + 2CH_2PhCl = (CH_2Ph)_2C_6H_3{\cdot}OH + PhOH + 2NaCl$, which, as a dissociating solvent, promotes the formation of *O*-alkyl derivatives from sodium phenoxides and alkyl halides (Claisen, *loc. cit.*; Busch, *Ber.*, 1927, **60**, 2244). Fraction (2) consisted of a light yellow, viscous oil which could not be induced to solidify. Analysis showed it to be a dibenzylphenol (Found: C, 87·4; H, 6·6. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%) and the orientation of the benzyl groups is indicated by the method of preparation and by comparison with the 2 : 4-isomeride. The *benzyl ether* of 2 : 6-*dibenzylphenol* was prepared by the interaction of the phenol (3·4 g.), sodium (0·3 g.), and benzyl chloride (1·5 g.) in solution in 95% alcohol (110 c.c.) at 100°. It crystallised from ligroin–methyl alcohol in colourless plates, m. p. 65° (Found: C, 88·9; H, 7·2. $C_{27}H_{24}O$ requires C, 89·0; H, 6·6%). The *α-naphthylurethane* of 2 : 6-dibenzylphenol was obtained by heating a mixture of α-naphthylcarbimide (1·3 g.) with the phenol (2·2 g.) almost to the b. p. for 3 minutes. The oily product was extracted with hot ligroin and filtered from the di-α-naphthylcarbamide. The product softened slightly at 161° and melted at 165—166° (Found: N, 3·3. $C_{31}H_{25}O_2N$ requires N, 3·2%).

4-*Hydroxydiphenylmethane*.—The method of van Alphen (*Rec. trav. chim.*, 1927, **46**, 803) was found to give poor yields and was therefore modified. Phenol (110 g.; 1·2 mols.) was condensed with benzyl chloride (126·5 g.; 1 mol.) in presence of anhydrous zinc chloride (2 g.) in the following manner. A mixture of the phenol, zinc chloride, and half the benzyl chloride was warmed gently until reaction set in, the remainder of the benzyl chloride was added in two portions at intervals of 1 hour, and the mixture was finally heated to 100° to complete the reaction. The product was dissolved in ether, washed with a small quantity of sodium

carbonate solution, dried, and fractionated at 10 mm. through a jacketed Vigreux column. The following fractions were separated: (1) 70—180° (75 g.), (2) 180—190° (70 g.), (3) 254—256° (31 g.). Fraction (1) consisted mainly of phenol. Fraction (2) contained 2- and 4-hydroxydiphenylmethane. A sharp separation of these two substances could not be effected by making use of the different solubilities of the barium salts (Friedr. Bayer Patentanmeldung 53443, 1923), but they were easily separated by taking advantage of the fact that the ortho-compound separates completely as a heavy oil as soon as a hot solution of the mixture in ligroin is cooled slightly. The pure para-compound (62 g., m. p. 84°) was deposited by the mother-liquor on cooling. Fraction (3) proved to be 2 : 4-dibenzylphenol and was identified by conversion into the α-naphthylurethane, m. p. 143—144° (see below).

2- *and* 4-*Benzyloxydiphenylmethane*.—These benzyl ethers were prepared by heating the phenol (8 g.), benzyl chloride (5·5 g.), and a solution of sodium ethoxide (from 1 g. of sodium) in 95% alcohol (300 c.c.) for 3 hours at 100°. The product was poured into water, extracted with ether, dried, and freed from the solvents.

2-*Benzyloxydiphenylmethane* may be recrystallised from warm methyl alcohol and melts at 38° (Found : C, 87·5; H, 6·7. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%). 4-*Benzyloxydiphenylmethane* crystallises from ethyl alcohol in glistening needles, m. p. 49·5° (Found : C, 87·6; H, 6·6%). These ethers are not hydrolysed by concentrated boiling hydrochloric acid or sodium hydroxide, but boiling hydriodic acid causes fission of the molecule with production of benzyl iodide.

2 : 4-*Dibenzylphenol*.—A solution of 4-hydroxydiphenylmethane (46 g.; 1 mol.) in dry toluene (200 c.c.) was added to sodium wire (5·8 g.; 0·8 mol.) immersed in 400 c.c. of toluene. The mixture was cautiously warmed, and a solution of benzyl chloride (31·7 g.; 1 mol.) in toluene (100 c.c.) added during 1 hour. The mixture was then slowly heated to the b. p. and boiled gently for 5 hours. The product was washed with water and sodium hydroxide solution, dried over calcium chloride, and freed from toluene. The residue was fractionated at 10 mm. and gave a pale yellow oil (25 g.; yield, 36%), b. p. 252—254° (Found : C, 87·3; H, 6·7. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%). The position of the benzyl groups was determined by fusion with potash. Dibenzylphenol (6 g.), potassium hydroxide (120 g.), and water (24 g.) were heated to 220°, and lead dioxide (22 g.) introduced during an hour. The product was lixiviated with water, filtered from litharge and resin, acidified, and extracted with ether. The solvent was removed and the residue distilled in a current of steam. The distillate contained benzoic acid (1·7 g., m. p. 122°). The residue was boiled with water and

passed through a hot filter to remove resinous material. The cream-coloured solid deposited by the filtrate on cooling was recrystallised from boiling water; *the acid obtained (0·05 g.) melted* at 308—309° and gave an intense cherry-red coloration with aqueous ferric chloride. The melting point of 4-hydroxy*iso*phthalic acid is 310° (Graebe and Krafft, *Ber.*, 1906, **39**, 798).

The benzyl ether, benzoate and diphenylurethane of 2 : 4-dibenzylphenol could not be induced to crystallise, but the *α-naphthylurethane* formed light yellow crystals (from ligroin), m. p. 143—144° (Found : N, 3·2. $C_{31}H_{25}O_2N$ requires N, 3·2%).

Identification of 4-Methoxydiphenylmethane.—This compound, which melts at 20—21° (Späth, *Monatsh.*, 1913, **34**, 2007), is liquid at atmospheric temperature and, since it was encountered during our experiments, we developed the following methods for its identification. (1) The methoxy-compound (5 g.) was demethylated in the usual way by heating for 1 hour with 58% hydriodic acid (12 g.). The resulting 4-hydroxydiphenylmethane melted at 84° after crystallisation from petroleum spirit. (2) Contrary to the statement of Rennie (J., 1882, **41**, 37, 227), the oxidation of 4-methoxydiphenylmethane with alkaline permanganate yields benzoic acid, and not 4-methoxybenzophenone, as main product. Oxidation with sodium dichromate and sulphuric acid also proved unsatisfactory and, after numerous trials, the following method, which gives a 56% yield of the desired product, was ultimately evolved.

4-Methoxydiphenylmethane (3 g.), dissolved in acetic acid (35 c.c.), was oxidised with chromic anhydride (7·9 g.) in the apparatus described by one of us (J., 1928, 2630). The product, isolated in the usual manner, was recrystallised from light petroleum and melted at 61—62°, which is the m. p. of 4-methoxybenzophenone recorded in the literature.

Rearrangement of Phenyl Benzyl Ether.—(A) Phenyl benzyl ether (70 g.) and zinc chloride (28 g.) were heated at 160° for 1 hour. The product was poured into water (200 c.c.), and extracted with ether, and the solution dried. After the solvent had been removed, the residue was distilled at 10 mm. and the following fractions were collected : (1) 73—78° (16 g.), (2) 160—180° (22 g.), (3) 240—260° (27 g.). Fraction (1), most of which distilled at 75°, consisted of phenol (benzoate, m. p. 68°). Extraction of fraction (2) with alkali removed 2- and 4-hydroxydiphenylmethane and left phenyl benzyl ether (3 g., m. p. 39°). The mixture of hydroxydiphenylmethanes contained 6 g. of the *o*-compound (benzyl ether, m. p. 38°) and 13 g. of the *p*-compound (m. p. 84°). *Fraction (3) consisted of 2 : 4-dibenzylphenol* (α-naphthylurethane, m. p. 143—144°).

(B) Phenyl benzyl ether (60 g.) was heated at 100° for 3 hours with anhydrous zinc chloride (2 g.), a slow stream of dry hydrogen chloride being passed through the liquid, which was stirred mechanically. A rapid current of steam was passed through the mixture for a few minutes and phenol (8 g.) was recovered from the distillate. The residue, when treated as described under (A), yielded 4-hydroxydiphenylmethane (17 g., m. p. 84°), 2 : 4-dibenzylphenol (9 g.), and resinous material (22 g.).

(C) Phenyl benzyl ether (40 g.) was heated at 100° for 3 hours, a slow stream of dry hydrogen chloride being passed through the liquid, which was stirred mechanically. The product was diluted with water, neutralised with sodium bicarbonate, and extracted with ether. The solution was dried, freed from the solvent, and distilled. The following fractions were collected: (1) 82—84°/ 15 mm. (13·5 g.), (2) 180—184°/10 mm. (8 g.), (3) 220—240°/2 mm (5 g.). Fraction (1) yielded to sodium hydroxide 10 g. of pheno and the residue was identified as benzyl chloride by oxidation t benzoic acid (m. p. 122°). Solution of fraction (2) in light petroleun resolved it into 2-hydroxydiphenylmethane (3 g.; benzyl ethe m. p. 38°) and 4-hydroxydiphenylmethane (5 g.; m. p. 84° Fraction (3) consisted of 2 : 4-dibenzylphenol (α-naphthylurethane m. p. 143—144°).

Condensation of Anisole and Phenol with Benzyl Chloride.—Anisol (43·2 g.; 1 mol.), phenol (37·7 g.; 1 mol.), and anhydrous zin chloride (1 g.) were heated to 100° and a slow stream of dry hydroge chloride was passed through the vigorously agitated liquid. Benz chloride (50·6 g.; 1 mol.) was introduced in small portions durin 20 minutes, and heating was continued for a total period of 3 hour The product was diluted with ether and extracted with moderatel concentrated sodium hydroxide solution, to which it yielded phen and the two hydroxydiphenylmethanes. The ether retaine anisole, 4-hydroxydiphenylmethane, dibenzylanisole, and th cryptophenolic 2 : 4-dibenzylphenol. Each of these mixtures w systematically fractionated under diminished pressure. In th way, phenol (25 g.), 2-hydroxydiphenylmethane (5 g.), ar 4-hydroxydiphenylmethane (12 g.) were separated from the alka soluble portion: they were identified as described in the previo sections. The alkali-insoluble mixture could easily be resolved in anisole (27 g.), 4-methoxydiphenylmethane (21·7 g.; b. p. 172 174°/10 mm.; identified by oxidation to 4-methoxybenzophenor m. p. 61—62°), and a mixture (8·5 g.; b. p. 240—260°/10 mm.) 2 : 4-dibenzylphenol and 2 : 4-dibenzylanisole. It was fou impracticable to separate this mixture into its constituents fractionation. A portion of it was demethylated with 58% hydrio

acid and the product gave an excellent yield of the α-naphthylurethane (m. p. 143—144°) of 2 : 4-dibenzylphenol. This indicated the constitution of the mixture, and a quantitative determination of the methoxy-content showed the presence of 23% of dibenzylanisole.

Rearrangement of Phenyl Benzyl Ether in Presence of Anisole.—Phenyl benzyl ether (73·6 g.; 1 mol.) and anisole (43·2 g.; 1 mol.) were heated to 100°, anhydrous zinc chloride (1 g.) was added, and a slow stream of dry hydrogen chloride passed through the liquid. At the end of 3 hours the product was worked up by the method already described. The alkali-soluble portion consisted of phenol (24 g.) and 4-hydroxydiphenylmethane (14 g., m. p. 84°). The alkali-insoluble products contained anisole (23 g.), 4-methoxydiphenylmethane (28·5 g.; identified by oxidation to 4-methoxybenzophenone, m. p. 61—62°), and a mixture (16 g., b. p. 240—255°/10 mm.) of 2 : 4-dibenzylanisole and 2 : 4-dibenzylphenol. The product obtained by demethylating a portion of this mixture gave a high yield of the α-naphthylurethane (m. p. 143—144°) of 2 : 4-dibenzylphenol. A methoxy-determination showed that the mixture in question contained 21% of dibenzylanisole.

Quinol Monomethyl Ether and Benzyl Chloride.—Quinol monomethyl ether, m. p. 56° (Robinson and Smith, J., 1926, 393) (8 g.), mixed with benzyl chloride (9 g.) and anhydrous zinc chloride (1 g.), was warmed until reaction set in and finally maintained at 100° for 0·5 hour. The product was taken up in ether and extracted with alkali. The alkali-soluble products were distilled and the following fractions collected: (1) 120—165°/10 mm. (3 g.), (2) 190—240°/10 mm. (6 g.). A small quantity of high-boiling yellow oil was not distilled. Fraction (1) solidified on cooling and consisted of unchanged quinol monomethyl ether. The majority of fraction (2) distilled at 200°/10 mm. and solidified on cooling. It was recrystallised from ligroin until a constant m. p., *viz.*, 77°, was attained (Found: C, 78·6; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). As the relative directive power of the hydroxy-group is superior to that of the methoxy-group, this product must be 2-*hydroxy*-4-*methoxydiphenylmethane*. This result agrees with the observation (Irvine and Smith, J., 1927, 74) that quinol monomethyl ether gives a homogeneous monobromination product.

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AUCKLAND UNIVERSITY COLLEGE,
UNIVERSITY OF NEW ZEALAND. [*Received, December 6th*, 1928.]

halogen) are less readily obtained (through, *e.g.*, the Grignard reaction) than are those of the type MR_3X when intermediate hydroxylation is involved in the method of isolation.

Another crystalline, deeply coloured, complex *iodide* was isolated (see Experimental) in small quantities during the present work. This was $Me_3TeI,2Me_2TeI_2$ (VI), which forms permanganate-coloured crystals. It is less stable than the " β-di-iodide " towards organic solvents.

An examination of the behaviour of the β-base with hydrobromic acid confirmed the previous deduction as to its nature. Colourless, crystalline *trimethyltelluronium bromide*, $TeMe_3Br$ (VII), was produced, together with a white substance identical with (II), which, on treatment with hydrobromic acid, yielded a yellow crystalline substance, *methyltelluronium tribromide*, $TeMeBr_3$ (VIII), soluble in ether. These two bromides, (VII) and (VIII), combined together in molecular proportion to give Vernon's " β-dibromide," identity being proved by a mixed melting point and a comparison of the general properties of the substances prepared in the two ways.

A small proportion of the α-base always accompanied the freshly isolated telluracetic acid, and the proportion of α-base increased when the product was kept in a desiccator for some weeks. It is probable, therefore, that telluracetic acid tends continually to change to a mixture of the α-base and tellurous acid, by the further wandering of a methyl group :

$$2MeTeO{\cdot}OH \longrightarrow Me_2Te(OH){-}O{-}TeO{\cdot}OH \xrightarrow{H_2O} Me_2Te(OH)_2 + TeO(OH)_2.$$

This is borne out by the fact that telluracetic acid, like the α-base and the α-dihalides, has a persistent odour of dimethyl telluride.

The α-base therefore tends towards an ultimate degradation to the most acid and the most basic substance possible, *viz.*, tellurous acid and trimethyltelluronium hydroxide :

$$3TeMe_2(OH)_2 = 2TeMe_3{\cdot}OH + Te(OH)_4.$$

Mixed " β-Dihalides."—To answer a possible objection that the " β-dihalides " might be formed by a rearrangement according to the equation $TeMe_3X + TeMeX_3 = 2TeMe_2X_2$, it was sought to prepare " β-dihalides " containing mixed halogens. This object was readily achieved. The appearance and properties of the mixed " β-dihalides " show that they belong to the same family as Vernon's β-dihalides, with which they form a series showing gradation of colours in crystals deposited, under uniform conditions, from acetone–chloroform solution. They are homogeneous substances, unaltered by further crystallisation. The series was :

$TeMe_3I,TeMeI_3$: purple-black, with green lustre;
$TeMe_3Br,TeMeI_3$: purple-red, with golden lustre;
$TeMe_3I,TeMeBr_3$: orange-brown;
$TeMe_3Br,TeMeBr_3$: yellow.

It is clear that the halogens of both components contribute to the colour of each salt, even although the components $TeMe_3X$ are themselves colourless. The colour, however, is seen to be governed mainly by the halogens of the component $TeMeX_3$, which are in excess.

The components reacted to form the salts when ground together even in the absence of solvents. This and the foregoing observations with regard to the colour changes show that the $TeMe_3X$ components possess each a mobile halogen atom, probably functioning as a mobile anion; and it becomes highly probable that the salts are correctly represented by the general formula $Me_3\overset{+}{Te}\cdots\overset{-}{Te}MeX_4$, equivalent to the co-ordination formula $[Me_3Te]TeMeX_4$, in which all the halogens and alkyl groups are covalently linked to tellurium. The negatively charged tellurium atom is thus associated with 58 electrons, if singlet linkings are assumed to be absent.

This view received support from the fact that a mixture * of acetone solutions containing equimolecular proportions of the " β-di-iodide " and potassium iodide, respectively, gives a precipitate of pure trimethyltelluronium iodide. The red filtrate, diluted with chloroform, gives a black *substance* which is probably the salt $[\overset{-}{Te}MeI_4]\overset{+}{K}$, since it is dissociated by moisture into potassium iodide and methyltelluronium tri-iodide.

Vernon's molecular-weight determinations of his β-dihalides in acetone and in nitrobenzene gave figures which were considerably higher than those demanded by his theory in the case of the iodide and the bromide, but not for the chloride. These results indicate that the salts are more readily ionised when $X = Cl$ than when $X = Br$ or I. Conductivity measurements of the salts in certain organic solvents are being carried out.

A less probable alternative general formula for the " β-dihalides " is $[Me_3\overset{+}{Te}\cdot TeMeX_3]\overset{-}{X}$, which differs from the first formula only as regards the position taken up by a single electron.

It was observed that such halides as ferric chloride and stannic bromide form coloured salts with trimethyltelluronium bromide or iodide. This suggests that there may be some analogy between the tellurium " β-dihalides " and the salts which the trisacetylacetone silicon, germanium, and titanium halides form with metallic chlorides,

* The author is indebted to Dr. N. V. Sidgwick for suggesting this test.

e.g., $[SiA_3]AuCl_4$, $[TiA_3]FeCl_4$, $[GeA_3]CuBr_2$. The possibility is thus presented of being able to replace the supposedly chelate acetylacetone radical (A) of the latter salts by univalent alkyl or aryl groups.

The assignment of a detailed formula to the triple salt (VI) must await further experimental evidence, but it may be noted that a salt of similar type occurs in the germanium series, *viz.*, $GeA_3Br,2CuBr$ (Morgan and Drew, J., 1924, **125**, 1261).

The α-dihalides possess marked solubility in light petroleum and other non-hydroxylic solvents, and are therefore to be regarded as distinctly non-polar substances, which, however, are capable of becoming ionised under exceptional conditions. If certain oxygen-containing radicals, such as HSO_4 and NO_3, were substituted for X, the resulting compounds would probably be typically polar (*e.g.*, $Me_2Te{<}^{SO_4H}_{SO_4H}$), *as first pointed out by the author* (*J.*, 1926, 3059). The α-dihalides show normal molecular weights in benzene and in acetone. They are reduced to dimethyl telluride by alkali bisulphites, and are regenerated from the telluride by the direct addition of halogens. These and other experimental results establish fairly conclusively a monomeric formula for the α-dihalides.

The central fact which results from the present work is, therefore, that the supposed isomerism of the dimethyltelluronium dihalides has no existence; and the same conclusion may be presumed to obtain for the diethyl and other homologues. Tellurium has, in all probability, not a plane, but a tetrahedral distribution of valencies.

Experimental.

The α-di-iodide, $TeMe_2I_2$, was prepared in the usual manner, and was recrystallised from chloroform, in which, contrary to Vernon's statement, it is quite stable (Found: C, 5·84; H, 1·46. Calc.: C, 5·84; H, 1·47%). It melts at 130°.

The β-base was prepared from this di-iodide as described by Vernon. The change of the α- to the β-base occurs in a vacuum at 95°, and the crystals of the latter appear to be stable for at least an hour at this temperature. When the filtered solution was treated with hydriodic acid, the precipitate obtained was manifestly non-homogeneous, a black tar (subsequently solidifying) and red crystals separating at different stages. The whole, when dissolved in acetone and precipitated by chloroform, gave glistening crystals of Vernon's β-di-iodide, which were either (*a*) deep purplish-red (Found C, 6·04; H, 1·61%) or (*b*) bronzed greenish-black (Found: C, 5·97 H, 1·78%). Since the two varieties can be obtained from the same solution by precipitation under slightly different conditions, they

are probably the same substance. Each gives a reddish-purple streak, and the purple powder becomes black (decomposition) between 80° and 85°. The substance was almost insoluble in chloroform and most non-hydroxylic solvents.

When the β-di-iodide (1 part) was warmed with aqueous sodium carbonate (0·78 part), a chocolate-coloured precipitate (A) was produced, which, when dissolved in boiling water and precipitated by hydriodic acid, gave a black substance. The latter, extracted with warm chloroform, yielded a small quantity of the pure α-di-iodide. The filtrate from (A), on the addition of hydriodic acid, gave a black precipitate (B). This was removed, and the filtrate slowly deposited a beautifully crystalline *substance* (VI), resembling potassium permanganate in colour and partly soluble in hot chloroform (Found: C, 7·47; H, 1·94. $TeMe_3I,2TeMe_2I_2$ requires C, 7·48; H, 1·89%). The black *substance* remaining from (B) could not be crystallised. It was dried and analysed (Found: C, 5·3; H, 1·35. $TeMe_3{\cdot}O{\cdot}TeI_3$ requires C, 5·2; H, 1·3%).

Small quantities of the α-di-iodide are also produced when the β-di-iodide is treated with boiling water alone, or with aqueous potassium metabisulphite, and then with hydriodic acid. This is probably due, not to reversion of the β-base to the α-base, but to one of the mechanisms already discussed. A small quantity of tellurium tetraiodide also appears to be formed by the action of hot water.

The β-base was next prepared on a larger scale, and precaution was taken, by twice evaporating the filtered solution in a vacuum, to obtain it free from α-base. A portion tested with hydriodic acid gave the usual blackish-red precipitates, which yielded the pure β-di-iodide on recrystallisation. Finally the β-base (from 5 g. of α-di-iodide) was dissolved in about 30 c.c. of water and the vigorously stirred solution was treated with freshly distilled, diluted, colourless hydriodic acid (4·6 c.c. of 11·4% HI required), added drop by drop until the liquid seemed nearly neutral to litmus. Each drop produced a red precipitate, which redissolved when vigorously shaken, leaving the solution colourless. A few black and white specks separated and were removed. The liquid, left in a vacuum over sulphuric acid for 1—2 hours, gave glistening colourless crystals of almost pure trimethyltelluronium iodide (I), of which two crops were obtained (total, 0·69 g.) (Found: C, 12·06; H, 2·98. Calc.: C, 12·03; H, 3·00%). This crystallised readily from hot water in long needles or in large flat prisms. It decomposed slowly above 240°, and disappeared rapidly at 248°, forming probably dimethyl telluride and methyl iodide. Its aqueous solution was neutral to litmus and gave no coloration or precipitate with hydrochloric acid or with colourless hydriodic acid.

The filtrate from this substance, when allowed to evaporate to dryness in the desiccator, gave an almost colourless, crystalline cake (1·30 g.). This was a mixture of the foregoing substance with a less soluble substance, which, however, tends to remain in supersaturated solution when once dissolved. The remaining trimethyltelluronium iodide was therefore removed from the mixture by gradual extraction with small quantities of hot water. The residue of white powder consisted of an *anhydride* of *methyl hydroxytellurium oxide* (*telluracetic acid*) (II), which could not be obtained pure. It appears to exist in several states of complexity, samples showing varying solubility in water. In aqueous solution, however, all were neutral to litmus, gave no precipitate with silver nitrate, and were reduced by potassium bisulphite to dimethyl ditelluride. Three separate preparations were analysed (Found : C, 7·6, 7·8, 7·7; H, 2·3, 2·0, 2·3. TeMeO·O·TeMeO requires C, 7·2; H, 1·8%). The substance, which had a persistent odour, did not melt but became gradually black above 230°. It was dissolved in boiling water and into the clear cooled solution was stirred colourless hydriodic acid drop by drop, until the liquid was faintly yellow. A bright scarlet precipitate of *methyltelluronium tri-iodide* (III) was continuously produced, changing in a few seconds to a stable purplish-chocolate form. The dried crystalline powder (Found : C, 2·38; H, 0·65; I, 72·4. $TeMeI_3$ requires C, 2·29; H, 0·57; I, 72·8%) closely resembled pure indigo in appearance. It dissolves in acetone or ether, giving bright red solutions, and from the former it is slowly precipitated by chloroform, as purple-black needles. It is only sparingly soluble in chloroform or glacial acetic acid. It is hydrolysed by boiling water or dilute hydriodic acid and is reprecipitated on cooling. It slowly decomposes above 100° and evolves gas near 130° and again at 180° (melting), leaving a black residue : much of its iodine is liberated in the free state when it is heated in oxygen.

Synthesis of Vernon's β-Di-iodide.—Trimethyltelluronium iodide and methyltelluronium tri-iodide were intimately mixed in exactly molecular proportion. Both dissolved on being warmed with a little acetone, although the former alone is insoluble in that solvent. The red solution, diluted with chloroform, gave at once the pure β-di-iodide in lustrous greenish-black scales or thin hexagonal plates (Found : C, 5·91; H, 1·52. Calc. : C, 5·84; H, 1·47%). From the mother-liquor a small further crop of the β-di-iodide was obtained in the purple-red form. The total yield seemed to be almost quantitative. Both forms, when powdered, became black at about 83°, and were in every respect identical with the forms obtained directly from the β-base.

Action of Hydrobromic Acid on the β*-Base.*—When the β-base (from 10 g. of α-di-iodide) was dissolved in 20 c.c. of water and 7·2 c.c. of 9·8% hydrobromic acid were gradually added, a white precipitate (A) formed which redissolved completely at first but only partly later. The clear filtrate, concentrated in a vacuum to a syrup, yielded large crystals of *trimethyltelluronium bromide* (VII) (Found: C, 14·32; H, 3·66; Br, 31·38. $TeMe_3Br$ requires C, 14·26; H, 3·57; Br, 31·66%), together with a white amorphous powder (B).

Trimethyltelluronium bromide is readily soluble in cold water but almost insoluble in organic solvents. It separates from water or aqueous alcohol in massive, transparent, colourless tablets, slowly decomposing between 250° and 280°. The neutral solution in water contains bromide ions and gives no precipitate or coloration with colourless hydriodic acid. The compound unites with ferric chloride, giving a complex salt which crystallises in salmon-coloured needles. It gives a complex salt also with stannic bromide.

The powders (A and B), when dissolved in hot water, treated with hydrobromic acid, and extracted with ether, gave *methyltelluronium tribromide* (VIII) (Found: C, 3·07; H, 0·78; Br, 62·9. $TeMeBr_3$ requires C, 3·14; H, 0·79; Br, 62·7%), yellow needles easily soluble in ether or hydrobromic acid, but hydrolysed by water. The substance becomes discoloured from about 140°, rapidly near 150°, and the dark mass melts to a black effervescing tar at 156°. The yellow solution in acetone is not precipitated by chloroform.

The crude powders (A and B), which consist of an anhydride of methyltellurium trihydroxide, contain also a small proportion of dimethyltellurium oxide or its oxybromide, since small amounts of the α-dibromide (colourless crystals, m. p. 96—97°, readily soluble in ether. Found: C, 7·6; H, 1·9. Calc.: C, 7·6; H, 1·9%) are produced by the action of hydrobromic acid.

Synthesis of Vernon's β*-Dibromide.*—The trimethyl bromide and the methyl tribromide combined when dissolved in equimolecular proportion in a little acetone, the yellow solution giving, on dilution with chloroform, lustrous yellow spangles (Found: C, 7·61; H, 1·97. Calc.: C, 7·56; H, 1·89%), m. p. 142° (decomp.; softening from 136°), unchanged on admixture with the β-dibromide prepared as described by Vernon. That author described the colour of this substance as "orange," but the crystals obtained from acetone–chloroform solution are always sulphur-yellow.

Mixed "β*-Dihalides.*"—The following compounds were prepared from their constituents, precisely as described above for the β-di-iodide and β-dibromide:

(1) $TeMe_3I,TeMeBr_3$, lustrous, orange-brown, flat needles, forming felted masses; m. p. 120° (decomp.) with darkening and

softening from 115° (Found: C, 7·18; H, 1·78. $Te_2Me_4Br_3I$ requires C, 7·04; H, 1·76%). It was unaltered by recrystallisation from ethyl alcohol (Found: C, 7·3; H, 1·9%).

(2) $TeMe_3Br,TeMeI_3$, dark, purple-red spangles with golden lustre (Found: C, 6·39; H, 1·59. $Te_2Me_4BrI_3$ requires C, 6·19; H, 1·55%): this does not melt, but becomes black below 90°. When kept for a few weeks, the crystals change to a purple form, but recrystallisation from ethyl alcohol restores the original form.

Action of Potassium Iodide on the "β-Di-iodide."—Potassium iodide and the β-di-iodide in molecular proportion were dissolved separately in acetone, and the solutions mixed. Colourless crystals of pure trimethyltelluronium iodide were deposited at once (yield, 80%). The deep red filtrate was evaporated to dryness in a desiccator, the solid residue dissolved in a little cold acetone and filtered, and the filtrate fractionally precipitated with chloroform. The almost black precipitate at first obtained consisted of the *salt* $\overset{+}{K}[\overset{-}{TeMeI_4}]$ contaminated with free potassium iodide (Found: C, 1·2; H, 0·3. $TeMeI_4K$ requires C, 1·7; H, 0·4%), but later, the proportion of free potassium iodide increased and the final mother-liquor contained free methyltelluronium tri-iodide. The complex potassium salt was insoluble in dry ether, but soluble in alcohol, giving a reddish-brown solution. It was easily dissociated by moist solvents.

The experimental findings of Vernon, so far as they have been examined here, are confirmed. Two observations in the literature, however, require modification, *viz.* (*a*) that the β-dihalides give dimethyl telluride on reduction, and (*b*) that the same tellurone, $TeMe_2O_2$, is derived from both bases, and that halogen acids regenerate from it the β-dihalides.

Regarding (*a*), it was found that the product is an orange oil, with carbylamine odour quite distinct from that of dimethyl telluride. The oil is probably dimethyl ditelluride, produced from TeMeO·OH by the normal reaction, the other component of the β-base $TeMe_3$·OH, remaining unreduced.

As to (*b*), examination of the literature shows that the tellurone has never been characterised. Vernon may have mistaken for it a higher oxide of the β-base (new formulation), or a mixture of the true tellurone with this oxide. Further, in the formation of the tellurone from the α-base, the latter may have been partly transformed, by heating, to the β-base.

Finally, attempts to form molecular compounds from the following combinations of substances gave negative results:

(1) TeI_4 and α-$TeMe_2I_2$; (2) TeI_4 and $TeMe_3I$;
(3) TeI_4 + α-$TeMe_2I_2$ + $2MeTe_2I$.

On the other hand, α-$TeMe_2I_2$ and $TeMe_3I$ combined together, in the presence of hydriodic acid containing iodine, to form a complex which crystallised in thin steel-blue needles, often several inches long. This substance, which melts to a purple liquid near 80°, evolves iodine when warmed with water. It has probably the formula $TeMe_3I,TeMe_2I_2,TeMe_2I_4$ [*i.e.*, it is a polyiodide of (VI)], but an exact analysis was not obtained (Found: C, 6·4; H, 1·7; I, 62·3. Calc.: C, 6·1; H, 1·5; I, 64·6%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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LXXXIII.—*A New Method for Preparing Substituted Diphenylamines.*

By ARTHUR WILLIAM CHAPMAN.

SUBSTITUTED diphenylamines are frequently difficult to prepare, especially if the two groups attached to the nitrogen atom are different. Direct substitution in diphenylamine or one of its derivatives may be employed, but such reactions are limited in number and do not reveal the constitution of the product. Even Ullmann's method (*Annalen*, 1907, **355**, 312; compare also Gibson and collaborators, J., 1927, 247; 1928, 2204) has a restricted application, and the process of heating an aromatic amine with an amine salt is mainly useful for the production of diphenylamines similarly substituted in both nuclei.

The author has recently shown (J., 1925, **127**, 1992; 1927, 1743) that *N*-arylaryliminoaryl ethers (II), when heated at 200—300°, are converted quantitatively into acyl derivatives of the corresponding diphenylamines (III). In this conversion the migrating group becomes attached to the nitrogen atom by means of the nuclear carbon atom that was originally attached to the oxygen atom.

$$R'NH_2 \xrightarrow{R\cdot COCl} R\cdot CO\cdot NHR' \xrightarrow{PCl_5} \underset{(I.)}{R\cdot CCl{:}NR'} \xrightarrow{R''ONa}$$

$$\underset{(II.)}{R\cdot C(OR''){:}NR'} \xrightarrow{\text{heat}} \underset{(III.)}{R\cdot CO\cdot NR'R''} \xrightarrow{KOH} NHR'R''$$

It has now been found that the acyl compounds thus obtained can be hydrolysed readily with alcoholic potash to the corresponding diphenylamines in yields of about 80% of those calculated. The imino-ethers can be prepared easily from the corresponding amines ($R'NH_2$) and phenols ($R''OH$) through the anilideiminochlorides (I) (J., 1922, **121**, 1676). In the typical case of *N*-*p*-chlorophenyl-

benzimino-2 : 4 : 6-trichlorophenyl ether, the yields of anilide, anilideiminochloride, and imino-ether were respectively 53, 88, and 80% of the theoretical.

A convenient means is therefore available for preparing diphenylamines with similar or different substituents in the two nuclei and of known constitution. The presence of "negative" substituents in the phenol facilitates the rearrangement of the imino-ether, whereas in the amine their presence retards the change. It is therefore preferable, if the alternative amines and phenols are available, to employ the more acidic phenol and the more basic amine, so that the rearrangement may occur at the lowest possible temperature. The approximate time and temperature of heating required can be estimated from the known effects of substituents on the velocity of the change (J., 1927, 1750).

Hitherto, the constitution of Gnehm's tetrachlorodiphenylamine, first prepared by direct chlorination of diphenylamine in glacial acetic acid solution, has remained unknown (*Ber.*, 1875, **8**, 1040). In view of the method of preparation it was probably 2 : 4 : 2′ : 4′-, 2 : 4 : 6 : 2′-, or 2 : 4 : 6 : 4′-tetrachlorodiphenylamine. These three compounds were therefore synthesised respectively from 2 : 4-dichlorophenol and 2 : 4-dichloroaniline, 2 : 4 : 6-trichlorophenol and *o*-chloroaniline, and 2 : 4 : 6-trichlorophenol and *p*-chloroaniline, through the corresponding benzanilides, benzanilideiminochlorides, benzimino-ethers, and benzoyldiphenylamines. Comparison with Gnehm's compound left no doubt of its identity with the 2 : 4 : 2′ : 4′-derivative.

EXPERIMENTAL.

The imino-ethers were prepared from the corresponding iminochlorides and sodium phenoxides by the method described for the preparation of *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J. 1922, **121**, 1676). The imino-ethers and benzoyldiphenylamines al crystallised well from alcohol, in which they were moderately easily soluble when hot, but only sparingly soluble in the cold.

N-*o-Chlorophenylbenzimino-2 : 4 : 6-trichlorophenyl ether*, from benz-*o*-chloroanilideiminochloride and 2 : 4 : 6-trichlorophenol formed colourless plates or prisms, m. p. 99—100° (Found : Cl, 34·7 $C_{19}H_{11}ONCl_4$ requires Cl, 34·5%), and was converted by heating fo 2 hours at 250—270° into *benzoyl-2 : 4 : 6 : 2′-tetrachlorodipheny amine*, prisms, m. p. 131—132° (Found : Cl, 34·5%).

N-p-*Chlorophenylbenzimino-2 : 4 : 6-trichlorophenyl ether*, from benz-*p*-chloroanilideiminochloride and 2 : 4 : 6-trichlorophenol formed pale yellow leaflets, m. p. 121—122° (Found : Cl, 34·3% and underwent rearrangement into *benzoyl-2 : 4 : 6 : 4′-tetrachlor*

diphenylamine (needles, m. p. 154°. Found : Cl, 34·5%) in 2 hours at 250—270°.

N-2 : 4-*Dichlorophenylbenzimino*-2 : 4-*dichlorophenyl ether*, from benz-2 : 4-dichloroanilideiminochloride and 2 : 4-dichlorophenol, was obtained as a viscous oil that did not crystallise even after standing for several weeks, but underwent isomeric change into *benzoyl*-2 : 4 : 2′ : 4′-*tetrachlorodiphenylamine* (plates, m. p. 153—154°. Found : Cl, 34·7%) on heating at 280—300° for 2 hours.

Numerous preliminary experiments showed that benzoyldiphenylamine itself and its substituted derivatives were best hydrolysed as follows : The benzoyl compound (10 g.) was boiled under reflux with a mixture of potassium hydroxide (50 c.c. of 50% aqueous solution) and alcohol (125 c.c.), and hydrolysis was complete in 2 hours. The mixture was then evaporated to dryness on the steam-bath, extracted with water, filtered, and the residue washed with water and crystallised from alcohol.

2 : 4 : 6 : 2′-*Tetrachlorodiphenylamine* formed stout prisms, m. p. 87—88°, sparingly soluble in alcohol (Found : Cl, 46·1. $C_{12}H_7NCl_4$ requires Cl, 46·2%).

2 : 4 : 6 : 4′-*Tetrachlorodiphenylamine* was readily soluble in alcohol and crystallised in prisms, m. p. 63—64° (Found : Cl, 46·3%).

2 : 4 : 2′ : 4′-*Tetrachlorodiphenylamine* crystallised in fine needles, m. p. 141—142°, very sparingly soluble in alcohol (Found : Cl, 46·3%).

2 : 4 : 6-*Trichlorodiphenylamine*, prepared from its benzoyl derivative, formed plates, m. p. 43—44°, readily soluble in alcohol (Found : Cl, 39·1. $C_{12}H_8NCl_3$ requires Cl, 38·7%).

Chlorination of Diphenylamine.—A rapid current of dry chlorine was passed into a solution of diphenylamine (50 g.) in glacial acetic acid (250 g.) under a reflux condenser. The chlorine was completely absorbed, hydrogen chloride was evolved, the solution became hot, and after the flask and contents had gained 40 g. in weight, the solution began to fill with long needle-shaped crystals. It was allowed to stand for an hour and filtered. The residue (55 g.), consisting of practically pure 2 : 4 : 2′ : 4′-tetrachlorodiphenylamine (m. p. 136—138°), crystallised from alcohol to a constant m. p. of 141—142° (Gnehm gives m. p. 133—134°); its identity with the tetrachlorodiphenylamine obtained as above was established by analysis (Found : Cl, 46·3%) and by mixed melting-point determination. When the chlorination was continued until chlorine was no longer absorbed (gain in weight = 60 g.), another substance separated, sparingly soluble in alcohol, m. p. 138—139° (Found : Cl, 56·6. $C_{12}H_5NCl_6$ requires Cl, 56·6%). It was therefore a *hexachlorodiphenylamine*, probably the 2 : 4 : 6 : 2′ : 4′ : 6′-compound. The

orientation could not be confirmed, however, as all attempts to hydrolyse benzoyl-2 : 4 : 6 : 2′ : 4′ : 6′-hexachlorodiphenylamine (J., 1927, 1747) or to benzoylate the amine were unsuccessful, no doubt owing to the intense steric hindrance of the four ortho-chlorine atoms.

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LXXXIV.—*The Chemistry of the Three-carbon System. Part XX.* cyclo*Pentylideneacetone and* cyclo-*Pentylidenemethyl Ethyl Ketone.*

By ALFRED HENRY DICKINS, WILFRED EYNON HUGH, and GEORGE ARMAND ROBERT KON.

IN Part XVII (Dickins, Hugh, and Kon, J., *1928*, *1630*) it was shown that *cyclo*hexylideneacetone and its βγ-isomeride, and also the corresponding ethyl ketones, could be prepared in a state of purity and a quantitative study was made of their conversion into equilibrium mixtures.

$$\text{(I.)}\quad \begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>C{:}CH\cdot COR \qquad \begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\!\!>C\cdot CH_2\cdot COR\quad \text{(II.)}$$

$$(R = Me \text{ or } Et).$$

The present paper deals with the corresponding *cyclo*pentan derivatives (I and II), which are of considerable interest from th point of view of tautomerism. In the first place, in a number (instances (compare Kon and Nutland, J., 1926, 3101; Kon an Speight, *ibid.*, p. 2727) the point of equilibrium in *cyclo*pentai derivatives is different from that in the corresponding *cyclo*hexai compounds. Means of determining the exact point of equilibriu now being available, the compounds mentioned above appeared be well suited for the investigation of this problem. Again, Gol berg and Linstead (J., 1928, 2343) have shown that the conversi of *cyclo*pentylidene- and *cyclo*pentenyl-acetic acids into the equ ibrium mixture of the two proceeds very rapidly, compared wi that of the *cyclo*hexane analogues; this mobility is somewh unexpected, as the principal factor should be the nature of t activating group and this is the same in both cases. Substitue undoubtedly do influence mobility—a good example has lately be observed (Abbott, Kon, and Satchell, J., 1928, 2514)—but eve

the *cyclo*hexane acids are regarded as substitution products of the *cyclo*pentane compounds, the substituent methylene group is attached to the δ-carbon atom, or rather shared between the two δ-carbons; it is not in the direct vicinity of the three-carbon system itself and therefore would not be expected to produce an appreciable effect.

A substance thought to be *cyclo*pentenylacetone was obtained by one of us from calcium *cyclo*pentanediacetate (Kon, J., 1921, **119**, 810) and later synthesised by Kon and Linstead (J., 1925, **127**, 815); the ketone in both cases gave a mixture of two semicarbazones, and it is now clear that it consisted of a mixture of *cyclo*pentylidene- and *cyclo*pentenyl-acetone (I and II; R = Me). The physical properties recorded by Kon and by Kon and Linstead, which also support such a view, refer to the ketone regenerated from a *mixture* of semicarbazones, although an experiment was made (Kon, *loc. cit.*) showing that the ketone regenerated from the pure high-melting semicarbazone again gave a mixture of semicarbazones.

In the light of past experience it was thought preferable to start with the two ethyl ketones (I and II; R = Et). These were prepared, but as they could not be obtained free from esters, etc., they had to be isolated in the form of their semicarbazones, that of the αβ-compound (I) being the higher-melting and less soluble; a semicarbazido-semicarbazone also was isolated in small amount. The pure ketones regenerated from these semicarbazones had the physical properties to be expected of their structure.

The methyl ketones (I and II; R = Me) were somewhat more easily obtained pure, notably the αβ-compound. The semicarbazone obtained from this consisted almost entirely of the sparingly soluble, high-melting substance already obtained by Kon and by Kon and Linstead and cyclo*pentylideneacetone* (I) was regenerated from it seemingly unchanged. The ketone so obtained was, however, much more reactive towards alcoholic iodine chloride than the ketone purified by repeated distillation and was therefore partly "equilibrated," and this accounts for Kon's observation (*loc. cit.*) that a mixture of semicarbazones is obtained from the regenerated ketone. The preparation of the βγ-ketone (II) presented many difficulties and mixtures were obtained in spite of all precautions. The crude ketone is best purified by conversion into the semicarbazone and subsequent treatment of the regenerated ketone with aluminium amalgam: the product has a sharp boiling point and a high reactivity towards iodine chloride and gives the low-melting semicarbazone, already described by Kon, as the sole product. Hydrolysis of the semicarbazone leads to a ketone which

has physical properties closely approaching those of the βγ-ketone, but its iodine addition is low.

The equilibrium established between the two pairs of ketones was determined quantitatively by the method of Linstead and May (J., 1927, 2565) exactly as in the case of the *cyclo*hexane compounds. Either of the isomeric ethyl ketones gives a mixture containing about 89·5% of the αβ-ketone; but as the ketones used for the reference curves were regenerated from the semicarbazones, this value is probably not accurate (compare above), especially as the equilibrium is on the side of the αβ-compound; it is probably nearer 85% αβ.

The mobility of the system is extremely high and equilibrium is practically completely established at the end of 20 minutes in the presence of an equivalent of *N*-sodium ethoxide at 25°; and it is not surprising that the βγ-ketone undergoes the Michael reaction with great readiness.

The methyl ketones behave similarly: the equilibrium mixture in this case contains 84% of the αβ-compound, and this figure is regarded as trustworthy. The iodine additions of the equilibrium mixtures of ethyl and methyl ketones are very similar, and the difference in point of equilibrium is probably due to the partial equilibration of the αβ-ethyl ketone. The regenerated αβ-methyl ketone has a higher iodine addition than the equilibrium mixture and therefore must contain more than 16% of βγ-ketone. It is remarkable that isomerisation should proceed past the equilibrium point in this case, but the presence of an acid reagent in place of alkali doubtless materially alters the nature of the reaction and the point of equilibrium. A similar excess of βγ-ketone over the equilibrium amount is also obtained in the preparation of the ketone from calcium *cyclo*pentanediacetate: in a recent preparation, the ketone regenerated from the crude semicarbazone contained approximately 36% of the βγ-ketone; and that originally prepared (Kon, *loc. cit.*) must have contained a good deal more since the βγ-semicarbazone was obtained in some quantity in spite of its great solubility. The two methyl ketones are also obtained on heating an intimate mixture of calcium acetate and calcium *cyclo*pentenylacetate. The production of the "less stable" form in a pyrogenic reaction is perhaps attributable to its greater vapour pressure, leading to a different equilibrium in the vapour phase: a comparable case has lately been described by Jupp, Kon, and Lockton (J., 1928, 1638).

The mobility of the methyl ketones is so great that exact quantitative measurements could not be carried out under the conditions now adopted as standard; the equilibrium is practically

complete at the end of 20 minutes in the presence of *N*-sodium ethoxide at 25°.

The experiments suffice to show that both the ethyl and the methyl ketones are very much more mobile than the corresponding *cyclo*hexane derivatives (experiments on the mobility of *cyclo*-hexylideneacetone are now in progress and will shortly be described) and thus fall into line with Goldberg and Linstead's observations. The point of equilibrium of the *cyclo*pentane ketones is on the side of the αβ-form: this agrees with the results already obtained with other *cyclo*pentane derivatives (*loc. cit.*), although we cannot at present offer an adequate explanation of the fact.

An attempt was made to ascertain the point of equilibrium in *cyclo*pentylidene*cyclo*pentanone. The ketone was prepared both by the action of hydrochloric acid and of sodium ethoxide on *cyclo*pentanone and a specimen was regenerated from the pure semicarbazone, m. p. 223°. All the samples examined showed very much the same iodine addition; this was low (6—7%) and did not change appreciably on treatment with sodium ethoxide. The point of equilibrium, therefore, must lie very near the αβ-ketone, but it cannot be ascertained exactly until the unknown βγ-isomeride is prepared. Experiments with the related *cyclo*hexenyl*cyclo*-hexanone were even less conclusive, inasmuch as Linstead and May's iodometric method failed in this case: the ketone absorbed more than three times the theoretical quantity of the reagent in a few minutes.

EXPERIMENTAL.

cyclo*Pentylidenemethyl Ethyl Ketone* (I; R = Et).—The ketone was prepared from *cyclo*pentylideneacetyl chloride in the same way as the *cyclo*hexane analogue (Dickins, Hugh, and Kon, *loc. cit.*); a 30% yield of a crude ketonic fraction, b. p. 94—96°/15 mm., was obtained. This was treated with semicarbazide acetate and the crude semicarbazone was freed from adhering esters, etc., by washing with petroleum and recrystallised from methyl alcohol. A small portion was insoluble, m. p. 215° (decomp.), and was probably the *semicarbazido-semicarbazone* (Found: N, 30·5. $C_{11}H_{22}O_2N_6$ requires N, 31·1%). The soluble portion crystallised in long needles, m. p. 174° (Found: C, 61·3; H, 8·9. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·8%).

The ketone regenerated from the semicarbazone by means of oxalic acid had b. p. 96°/20 mm., $d_{4°}^{22·9°}$ 0·93179, $n_D^{22·9°}$ 1·47801, $[R_L]_D$ 41·96 (calc., 41·21), and gave a semicarbazone melting at 171° without recrystallisation.

Δ^1-cyclo*Pentenylmethyl Ethyl Ketone* (II; R = Et).—Δ^1-*cyclo*-Pentenylacetic acid, from which the ketone was ultimately synthes-

ised, was mostly prepared from its ester by Wallach's method (*Annalen*, 1906, **347**, 324; Kon and Linstead, J., 1925, **127**, 616). Another method, which yields a very pure product, consists in the dry distillation of *cyclo*pentylidenemalonic acid (Kon and Speight, *loc. cit.*) under reduced pressure. As the αβ-structure of the acid is unquestionable, having been again confirmed by us by oxidation with permanganate, this decomposition involves a shifting of the double bond into the ring.

The first attempt to prepare the ketone by the Blaise–Maire reaction led to the isolation of the αβ-semicarbazone, m. p. 174°. The mother-liquor, however, contained a small quantity of a more fusible substance; after repeated crystallisation, this formed needles, m. p. 135°.

*Δ^1-cyclo*Pentenylacetyl chloride (20 g.) was dropped into a well-cooled solution of zinc diethyl (10 g.) in dry ether, dry carbon dioxide being bubbled through the reaction vessel. On decomposing the product with ice, a ketonic substance (about 3 g.), b. p. 85—90°/19 mm., was obtained, but this gave the αβ-semicarbazone, m. p. 174°, as the sole product.

A slight excess of magnesium ethyl iodide in dry ether was added to a well-cooled ethereal solution of the acid chloride (20 g.); after decomposition with ice, about 3 g. of a ketonic substance were obtained, but this again yielded the αβ-semicarbazone. When the amide was substituted for the acid chloride, no ketonic product at all was obtained.

The best results were finally achieved by carrying out the Blaise–Maire reaction very slowly and using a very carefully fractionated acid chloride, b. p. 82°/19 mm. (the higher fraction generally contains the isomeric αβ-chloride). Even then the preparation failed sometimes for no apparent reason; the yield of ketone never exceeded 30% and a quantity of ester was always formed.

The *semicarbazone* melted at about 113°, but formed needles, m. p. 135°, after repeated crystallisation (Found : C, 61·4; H, 8·9. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·8%). The ketone regenerated from it had b. p. 90°/21 mm., $d_4^{22.5°}$ 0·92429, $n_D^{22.5°}$ 1·46509, $[R_L]_D$ 41·31 (calc., 41·21); it gave on recombination with semicarbazide a product, m. p. 134° after one crystallisation from methyl alcohol.

Condensation with Ethyl Sodiomalonate.—The ketone was condensed with ethyl sodiomalonate in alcoholic solution (compare Dickins, Hugh, and Kon, *loc. cit.*), and the resulting ester hydrolysed with barium hydroxide; the *cyclopentane*-spiro-*4-methyl*-cyclo*hexane*-3 : *5-dione* obtained on acidification crystallised from dilute methyl alcohol in needles, m. p. 174—175° (Found : C, 73·2; H, 8·9. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%).

Equilibrium between the Ethyl Ketones.—The quantitative analysis of mixtures of the two ketones was carried out iodometrically by the method of Linstead and May. A reference curve was constructed from the following values obtained with *M*/300-chloroform solutions in 10 minutes :

Mixture (% αβ) ...	*0*	*10*	*25*	*50*	*75*	*90*	*100*
Addition (%)	88·4	82·5	74·5	60·5	45·8	37·6	33·0

The addition of the αβ-ketone was unusually high, probably owing to partial equilibration during the hydrolysis of the semicarbazone (compare p. 573).

Point of equilibrium. The pure αβ-ketone was kept with a slight excess of alcoholic sodium ethoxide for 24 hours, then isolated and analysed iodometrically; it had an iodine addition of 37·9% (corresponding to 90% of αβ-ketone). The βγ-ketone was similarly treated; it had b. p. 101—103°/25 mm. and gave an addition value of 38·5% (corresponding to 89% of αβ-ketone); the equilibrium mixture thus contains approximately 89·5% of the αβ-ketone. As already explained, this figure is probably too high because any error due to the impurity of the αβ-ketone would have a considerable effect.

Mobility. The following experiments were carried out with the βγ-ketone : the ketone was kept with *N*-alcoholic sodium ethoxide (1 equiv.) at 25° and portions were isolated and analysed.

Time	20 mins.	40 mins.	24 hours
Addition (%)	39·6	39·0	37·9
αβ-Ketone (%)	87·0	88·0	89·9

Equilibrium is thus practically reached at the end of 20 minutes; shorter periods were not used owing to the scarcity of the material and the inevitably high experimental errors.

cyclo*Pentylideneacetone* (I; R = Me).—The ketone was prepared from *cyclo*pentylideneacetyl chloride in the same way as its higher homologue. The ketonic product on redistillation gave a small amount, b. p. 72—74°/12 mm., a large fraction, b. p. 74—75°/12mm., and another small one, b. p. up to 88°/12 mm. The lowest fraction gave a semicarbazone, m. p. 172—173° : on recrystallisation from methyl alcohol, needles, m. p. 185—186°, were obtained, identical with the high-melting form obtained by Kon and by Kon and Linstead (*locc. cit.*). The large fraction gave a somewhat higher-melting semicarbazone; the yield was rather poor. The ketone can be regenerated from the semicarbazone if a small quantity is employed. For instance, 3 g. of the pure compound, m. p. 189°, gave a ketone, b. p. 70°/12 mm., $d_4^{19\cdot9^\circ}$ 0·94205, $n_D^{19\cdot9^\circ}$ 1·47937, $[R_L]_D$ 37·16 (calc., 36·60) : the semicarbazone prepared from this

ketone had m. p. 174°, rising to 180—181° after one crystallisation. The regenerated ketone had an iodine absorption of 44·7% (in 5 minutes). Another sample prepared in the same way had an even higher molecular refraction (37·43), but the iodine addition was 45·8% (compare below).

The ketone was finally prepared by repeated fractionation of the crude ketonic product. It boiled at 74—76°/14 mm., its iodine addition was 27·8%, and its purity was proved by the fact that the equilibrated ketone obtained from it had approximately the same iodine addition as that obtained both from the regenerated ketone and from the βγ-isomeride.

cyclo*Pentenylacetone* (II; R = Me).—The preparation of this ketone was carried out exactly as described on p. 576. The yield of ketonic fraction, the b. p. of which was lower than in the preceding case, was poor. It gave a caseous semicarbazone from which the compound, m. p. 189°, could generally be obtained. The product of several preparations was combined and carefully redistilled, a fraction, b. p. 72—74°/15 mm., being obtained, $d_4^{17\cdot0^\circ}$ 0·95400, $n_D^{17\cdot0^\circ}$ 1·46569, iodine addition 73·3% (5 minutes). On treatment with aluminium amalgam (compare Hugh, Kon, and Linstead, J., 1927, 2585) this value rose to about 84%. A part of the crude ketone was therefore converted into the semicarbazone, which was very soluble in all solvents and to some extent even in water; it was purified by repeated grinding with light petroleum (b. p. 40—60°), and the ketone regenerated from it. This was dissolved in much ether and treated with aluminium amalgam in excess. After the reaction had continued for about 4 hours the ketone was isolated; it boiled at 69—70°/16 mm., had $d_4^{20\cdot4^\circ}$ 0·93568, $n_D^{20\cdot4^\circ}$ 1·46211, $[R_L]_D$ 36·58 (calc. 36·60), iodine addition 87·7%, and was evidently pure *cyclo*pentenylacetone. The semicarbazone prepared from it was the low-melting form obtained by Kon and by Kon and Linstead (*locc. cit.*); it melted at 129° without purification.

An attempt was made to prepare the ketone from the acid chloride by the Grignard reaction; the yield of ketonic product was very small and only the αβ-semicarbazone was obtained from it.

Ketone from Calcium cyclo*Pentanediacetate*.—Calcium *cyclo*pentanediacetate was distilled exactly as described by Kon (*loc. cit.*). The appropriate ketonic fraction was converted into the semicarbazone, which was ground with petroleum and hydrolysed with oxalic acid. The regenerated ketone had b. p. 66—70°/15 mm. $d_4^{19\cdot8^\circ}$ 0·93070, $n_D^{19\cdot8^\circ}$ 1·46420, iodine addition 51·8% (corresponding to 64% of αβ-ketone; see below).

A similar product was obtained by distilling an intimate mixture of calcium acetate and calcium *cyclo*pentenylacetate under the same

conditions. The ketone purified through the semicarbazone had b. p. 80—84°/24 mm., $d_{4°}^{19·2°}$ 0·93405, $n_D^{19·6°}$ 1·46847, iodine addition 47·8%.

Equilibrium between the Methyl Ketones.—The analysis of mixtures of the two ketones was carried out as in the previous case, but, owing to the high additive power of the ketones, 5 minutes was chosen as the standard time. A reference curve was constructed from the following values :

Mixture (% αβ) ...	0	10	25	50	75	90	100
Addition (%)	86·1	82·7	75·1	60·3	45·2	34·9	27·8

The αβ-ketone used for the reference curve was the specimen described above, purified by fractionation; the βγ-ketone was purified by regeneration and treatment with aluminium amalgam.

Point of equilibrium. The αβ-ketone (iodine addition, 44·7%; see p. 578) regenerated from the semicarbazone of m. p. 189° was kept with a slight excess of sodium ethoxide for 24 hours; the mixture became very dark. The ketone isolated had an iodine addition of 39·1% (corresponding to 84% of αβ-ketone) and gave an immediate precipitate of the semicarbazone, m. p. 189°, on treatment with semicarbazide. The fully equilibrated material thus contained more αβ-ketone than the regenerated αβ-ketone. Another specimen prepared in the same way (iodine addition, 45·8%) was treated for 3 hours only, *N*-sodium ethoxide being used; the ketone isolated had $d_{4°}^{20·0°}$ 0·93947, $n_D^{20·0°}$ 1·47751, and iodine addition 38·8% (corresponding to 84·5% of αβ-ketone). A separate experiment showed that the αβ-ketone purified by distillation only, gave the same equilibrium mixture as the regenerated material.

Only one experiment was performed with the βγ-ketone, *N*-sodium ethoxide being used; at the end of 3 hours the iodine addition fell to 35·9% (corresponding to 88·5% of αβ-ketone) and the mixture had $d_{4°}^{20·0°}$ 0·94190 and $n_D^{20·0°}$ 1·48005.

Mobility. The pure βγ-ketone was mixed with *N*-sodium ethoxide (1 equiv.) and kept in a thermostat at 25°; one half of the liquid was removed at the end of 10 minutes and poured into water containing the calculated amount of acetic acid, and the remainder was similarly treated at the end of 20 minutes. The ketones were isolated and analysed; the first portion had an iodine addition of 41·9% (corresponding to 80% of αβ-ketone), the second 41·2% (80·5% of αβ-ketone). The two portions were then combined and kept with a slight excess of sodium ethoxide for 1½ hours; when isolated, the ketone had an iodine addition of 39·2% (corresponding to 84% of αβ-ketone), thus confirming the point of equilibrium previously found. It will be seen that equilibrium is practically established at the end of 10 minutes.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, December 17th*, 1928.]

LXXXV.—*The Solubility of Iodine in Solutions of Halides.*

By JOHN STANLEY CARTER and CHARLES RANDALL HOSKINS.

MEASUREMENTS of the solubilities of certain non-electrolytes in solutions of electrolytes have shown that, in the absence of interaction between the two, the relation between the solubility s and the electrolyte concentration C is represented by the exponential equation $s = s_0e^{-aC}$, where s_0 has a value equal to or approximating to the solubility in the pure solvent and a is a constant which measures the salting-out effect of the electrolyte. When the non-electrolyte and the electrolyte react to form a soluble complex, the salting-out effect is opposed by a tendency towards increased solubility, and the solubility actually observed will depend on the relative magnitudes of the two opposing effects. If the equilibrium involved in the formation of the complex is known, it should be possible, by making allowance for the salting-out effect, to obtain constancy of the mass-law expression concerned.

Such a case has already been investigated in connexion with the solubility of iodine in solutions of sodium chloride [Dawson and Carter, *Proc. Leeds Phil. Soc.*, 1925, **1**, (i), 14; Carter, J., 1925, **127**, 2861]. Iodine dissolved in solutions of sodium chloride exists in part as free iodine and in part as the complex polyhalide $NaClI_2$, the influence of polyhalide formation being such that the solubility passes through a maximum as the concentration of sodium chloride increases. It was found possible to distinguish between the two opposing effects and to show that polyhalide formation was superimposed on the normal salting-out process.

The more comprehensive examination of this type of equilibrium now described includes measurements, not only of the solubility of iodine at 25° in solutions of simple halides, but also of the influence of certain inert salts. Bell and Buckley (*J. Amer. Chem. Soc.*, 1912 **34**, 10) determined the solubility of iodine in solutions of sodium and potassium bromides but did not attempt a quantitative interpretation; a representative selection from their data has therefore been recalculated on a weight-concentration basis and incorporated with the present measurements.

The equilibrium involved is $X' + I_2 \rightleftharpoons XI_2'$, where X = Cl, Br, or I. In the above equation, therefore, s is the concentration of free iodine, s_0 is its solubility in pure water, and a is at present unknown. If S is the observed solubility, the concentrations of the participants in the equilibrium involved are $[X'] = C - (S - s)$; $[I_2] = s$; $[XI_2'] = S - s$, and according to the mass-action law,

$$K = [C - (S - s)]s/(S - s) \quad . \quad . \quad . \quad . \quad (1)$$

By plotting against C the values of K obtained from the simple mass-law relation (ignoring the salting-out effect) and extrapolating to $C = 0$, we obtain a value K_0 which may be regarded as the true equilibrium constant. Now, from equation (1), if we assume that $S - s$ is small compared with C, we see that $S = s(1 + C/K)$; and putting the exponential relation in the form $\log_e s = \log_e s_0 - aC$ and eliminating s between these two expressions, we obtain as an approximation

$$a = 1/C \, . \log_e s_0(1 + C/K)/S,$$

the extrapolated value K_0 being assumed to be equal to K.

This approximation is permissible for chlorides and bromides, but not for iodides. The solutions of iodides used were, however, very dilute, and in view of the known low salting-out power of the iodide ion, the data for solutions containing iodides have been considered without reference to this effect; the experimental data show that the procedure is justified.

Having thus obtained the value of a, the value of s for any particular concentration may be determined from the exponential relation. Actually it was more convenient to convert this relation to its equivalent in Briggsian logarithms, *viz.*, $\log s = \log s_0 - a'C$, where $a' = a/2{\cdot}3$.

This procedure involves the assumption that halide and polyhalide have the same salting-out power. With both chlorides and bromides the proportion of polyhalides is extremely low and hence no appreciable error is thereby introduced. The data for the simple halides are collected in Table I. In accordance with previous practice all concentrations have been referred to a fixed weight of water and are expressed as mols. (equivs. in the case of magnesium and barium chlorides) per 1000 mols. of water. The value of s_0 is $2{\cdot}38 \times 10^{-2}$. The first column gives the concentration of halide, the second the observed solubility, the third the calculated concentration of free iodine, and the last the value of the mass-law constant calculated from equation (1).

The solubility data for hydrochloric acid are in excellent agreement with the solubility and partition measurements of Rây and Sarkar

TABLE I.

Hydrochloric acid, $a' = 0{\cdot}0005$.				Potassium chloride, $a' = 0{\cdot}0032$.			
C.	100 S.	100 s.	K.	C.	100 S.	100 s.	K.
8·48	4·31	2·36	10·3	6·15	3·49	2·27	11·4
17·9	6·55	2·33	9·9	12·3	4·38	2·17	12·1
25·1	7·93	2·31	10·3	24·6	5·89	1·99	12·6
31·5	9·51	2·29	10·0	36·3	7·11	1·82	12·5
65·3	17·0	2·21	9·8	48·2	8·22	1·67	12·3
79·5	19·7	2·17	9·8	60·6	9·05	1·52	12·2
109·2	25·2	2·10	9·9	73·9	9·75	1·38	12·2
141·0	29·9	2·02	10·2	86·8	10·03	1·26	12·5
Magnesium chloride, $a' = 0{\cdot}0055$.				Barium chloride, $a' = 0{\cdot}0058$.			
8·48	3·94	2·14	10·1	3·67	3·05	2·27	10·7
13·0	4·65	2·02	10·0	4·89	3·18	2·23	11·5
26·3	6·34	1·71	9·7	12·1	4·26	2·03	11·0
53·5	7·41	1·21	10·4	24·0	5·38	1·73	11·4
67·5	7·50	1·01	10·5	35·6	6·10	1·48	11·4
96·1	7·32	0·70	10·2	46·9	6·60	1·27	11·2
125·9	6·36	0·48	10·3	57·8	6·76	1·10	11·2
141·3	5·73	0·40	10·6	68·6	6·71	0·95	11·3
*Sodium bromide, $a' = 0{\cdot}0042$.				*Potassium bromide, $a' = 0{\cdot}0015$.			
C.	10 S.	100 s.	K.	C.	10 S.	100 s.	K.
16·9	2·449	2·02	1·49	16·8	2·598	2·25	1·57
34·5	4·009	1·70	1·51	37·8	5·165	2·09	1·57
68·6	5·955	1·23	1·44	65·2	8·155	1·90	1·54
83·0	6·491	1·07	1·38	82·9	10·06	1·79	1·47

Hydriodic acid, $a' = 0$; $s = s_0$.

10 C.	10 S.	100 K.	10 C.	10 S.	100 K.
2·117	1·326	2·25	13·21	2·908	2·33
5·284	2·956	2·25	17·63	9·228	2·29
8·810	4·715	2·30	49·64	27·84	1·90

* Calculated from Bell and Buckley's values (see p. 580).

(*J.*, 1922, **121**, 1449) for dilute solutions, the value of K calculated from their data being 10·8.

Consideration of the data for the chlorides shows that when a' is very small the solubility increases almost linearly with the concentration of electrolyte. When the value of a' is considerable, the observed solubilities are smaller and show maximum values. Potassium chloride shows no maximum, but the curve is considerably flattened at high salt concentrations.

Bell and Buckley have shown that the solubility in solutions of sodium bromide is maximal at a high salt concentration ($C = 120$). Potassium bromide shows no maximum, nor is the solubility curve particularly flattened at high concentrations.

In view of the number and nature of the assumptions involved and the considerable range of electrolyte concentration, the agreement amongst the values in the last column of each section is satisfactory. The values of K indicate that the combining power of the halogen ion is not entirely independent of the associated kation. The

values of a' are in good agreement with those anticipated from considerations of the available data on the salting-out effect.

From the data for hydriodic acid, it is seen that K is approximately constant for dilute solutions, but, as the last determination shows, tends to decrease at higher concentrations, probably as the result of the formation of higher polyiodides. This behaviour is in agreement with the existing data on the solubility of iodine in solutions of iodides.

It is interesting to compare the a' and K values for the three halogens. Taking the sodium salt as representative, we find for K, chloride, 12·0; bromide, 1·45; iodide, 0·025, and for a', chloride, 0·00575; bromide, 0·0042; iodide, nil. These values indicate that the tendency to form polyhalides increases and the salting-out power decreases with increasing atomic weight.

Attempts were made to determine the solubility of iodine in solutions of fluorides. It was found, however, that the solubility increased with the period of agitation, due to reaction between iodine and fluoride with production of iodide and development of acidity. The solubility measurements were therefore abandoned, but it is hoped to investigate this particular reaction in the future.

Influence of Inert Salts.—The following data refer to the changes in solubility at 25° due to the addition of inert salts when the concentration of halides remains fixed. The salts chosen were sodium nitrate and sulphate, the appropriate values of a' (*viz.*, 0·00296 and 0·0180 respectively) being taken from an earlier paper. Under the experimental conditions, the salting-out in the case of solutions containing iodides is entirely due to the added salt only; but with solutions containing bromide, this is in some degree responsible for the salting-out. To determine the magnitude of the latter effect, it was assumed that the bromide present had the same effect as an amount of sodium sulphate equal to the concentration of bromide multiplied by the ratio of the a' values concerned. Thus, 9·25 mols. of sodium bromide $= 9{\cdot}25 \times 0{\cdot}0042/0{\cdot}0180 = 2{\cdot}16$ mols. of sodium sulphate. The first column of Table II gives the concentration of added salt, the second the observed solubility, the third the calculated concentration of free iodine, and the last the value of K according to the mass-law expression. All concentrations are expressed as mols./1000 mols. of water.

A consideration of the data shows that the value of K is not constant: with bromide it decreases, and with iodide it passes through a maximum. The value undergoes no serious variation, however, and in view of the assumptions made and the high salt concentrations involved, the approximate constancy cannot be regarded as other than satisfactory. The numbers show that

TABLE II.

Sodium bromide–sodium sulphate.

[NaBr] = 9·245;
$\log s = \log s_0 - 0{\cdot}018([Na_2SO_4] + 2{\cdot}16)$.

$[Na_2SO_4]$.	100 *S*.	100 *s*.	*K*.
0·00	16·02	2·18	1·43
6·42	12·48	1·67	1·41
12·84	9·82	1·28	1·37
19·26	7·60	0·979	1·36
25·68	5·97	0·751	1·32

Sodium iodide–sodium nitrate.

[NaI] = 0·4938;
$\log s = \log s_0 - 0{\cdot}00296[NaNO_3]$.

$[NaNO_3]$.	10 *S*.	100 *s*.	100 *K*.
0·0	2·670	2·38	2·45
12·0	2·526	2·19	2·50
24·0	2·383	2·02	2·55
36·0	2·230	1·86	2·63
48·0	2·087	1·72	2·71
60·0	1·957	1·58	2·76
120·0	1·480	1·05	2·72
180·0	1·131	0·698	2·55

Sodium iodide–sodium sulphate.

[NaI] = 0·4938; $\log s = \log s_0 - 0{\cdot}0180[Na_2SO_4]$.

$[Na_2SO_4]$.	10 *S*.	100 *s*.	100 *K*.
6·0	2·290	1·86	2·50
12·0	1·938	1·45	2·54
18·0	1·630	1·13	2·55
24·0	1·411	0·880	2·40
30·0	1·179	0·686	2·37

sodium sulphate is about five times as efficient as sodium nitrate in repressing the tendency to form tri-iodide.

It is interesting to compare some of our mean values of *K* for chloroiodides with those for corresponding chlorobromides, obtained with relatively dilute solutions by partition measurements, and recalculated to our units of concentration (all the data relate to 25°, except that for $HClBr_2$ which relates to 30°):

	$HClI_2$.	$KClI_2$.	$MgCl_2I_4$.	$BaCl_2I_4$.	$HClBr_2$.	$KClBr_2$.	$MgCl_2Br_4$.	$BaCl_2Br_4$.
K	10·0	12·2	10·2	11·2	12·8*	13·1†	13·0‡	13·1‡

* Rây and Sarkar, *loc. cit.* † Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19.
‡ Dancaster, J., 1924, **125**, 2038.

From an examination of the above it is apparent that the chloro-dibromides and -di-iodides are dissociated to approximately the same extent, the latter being slightly more stable. The *K* value for $HClBr_2$ at 25° would be somewhat lower than that at 30°; it is thus seen that the *K* values for the acids are, in general, somewhat lower than those for the corresponding salts, indicative of the greater stability of the acid complexes. Similar behaviour is observed with the tri-iodides, the *K* values at corresponding concentrations being $2{\cdot}25 \times 10^{-3}$ for acid and $2{\cdot}45 \times 10^{-3}$ for the sodium salt. Jakowkin (*loc. cit.*) and Dawson (J., 1901, **79**, 238) obtained similar results by partition measurements.

Experimental.—Iodine was purified by customary methods and the electrolytes used were of good quality. The usual precautions were taken in determining solubilities.

Conclusions.

The data presented may be said to have established the fact that the solubility of iodine in solutions of halides is the result of two opposing effects—the tendency to form polyhalides and the simple salting-out effect. The observed solubility is dependent on the relative magnitude of these effects. With iodides the salting-out effect is negligible, but with bromides and especially with chlorides it is of considerable importance. These considerations do not apply to the halogen acids, which possess little or no salting-out action. It has, however, been shown in numerous investigations of the salting-out effect that the behaviour of acids is quite different from that of the corresponding salts, so the preseut anomaly is scarcely surprising.

Brönsted and Pedersen (*Z. physikal. Chem.*, 1923, **103**, 307) have made some measurements of the tri-iodide equilibrium by the solubility method, using as solvent a 1·65N-potassium chloride solution, and their value for the mass-law expression has been not infrequently quoted and used by others These authors assumed that iodine dissolved in the aqueous solution of potassium chloride is entirely present as free iodine. Their K value is therefore considerably in error. When suitable corrections are made for the disturbing effect of polyhalide formation, it is found that the resulting value of K is approximately the same as when the solvent is water.

Our thanks are due to the Government Chemist, Sir Robert Robertson, F.R.S., for providing facilities for the work to be carried out and for permission to publish these results.

The Government Laboratory,
London, W. C. 2. [*Received, January 16th*, 1929.]

NOTES.

Elimination of the Nitroso-group from Nitrosoamines. By William George Macmillan and Thomas Harold Reade.

The usual method of eliminating the nitroso-group of a nitrosoamine by dissolution in concentrated hydrochloric acid often leads to mixtures from which the secondary amine is obtainable only with difficulty, particularly when there is hydrogen in the para-position with respect to the nitrosoamine group. To facilitate elimination of the nitroso-group, different substances capable of

decomposing nitrous acid have been used with varying degrees of success. In sulphuric acid, glycine, acetamide, and potassium cyanate or thiocyanate are useless, but urea and thiourea work admirably and this method of elimination can be recommended for its rapidity and simplicity. For example, on addition of 20 g. of *m*-nitrophenylmethylnitrosoamine to 15 g. of urea in 75 c.c. of water and 75 c.c. of sulphuric acid at 50°, instantaneous evolution of gas (nitrogen, carbon dioxide, and nitric oxide) took place. This was completed by heating for 15 minutes at 100°.

After cooling, precipitation by ammonia, and crystallisation from ligroin, the *m*-nitromonomethylaniline obtained (15·5 g.), m. p. 67·5° (Ullmann, *Annalen*, 1903, **327**, 112, gives m. p. 65—66°) (Found: C, 54·9; H, 5·9; N, 18·0. Calc.: C, 55·2; H, 5·3; N, 18·4%), failed to give Liebermann's nitrosoamine reaction and was reconverted by nitrous acid into the nitrosoamine (1·8 g. from 2·0 g. of base). The yields of secondary amine obtained varied from 90 to 95% from the *m*-compound and from 80 to 90% from *p*-nitrophenylmethylnitrosoamine. With thiourea a similar procedure gave equally satisfactory results, no experiment giving less than 80% or more than 95% of recrystallised secondary amine.

Nuclear nitroso-compounds, *e.g.*, *p*-nitrosodimethylaniline and α-nitroso-β-naphthylamine, were recovered unchanged.—UNIVERSITY OF ABERDEEN. [*Received, February 9th*, 1929.]

The Preparation of p-*Azoxyanisole and Derivatives.* By WILLIAM DAVIES and RALPH ALEXANDER RODGER DOWN.

THE two-fold action of sodium methoxide in the production of azoxyanisoles from *p*- and *o*-halogenonitrobenzenes has been recorded by Jackson and Fiske (*Ber.*, 1902, **35**, 1131) and Brand (*J. pr. Chem.*, 1903, **67**, 150).

In the preparation of *p*-azoxyanisole from *p*-chloronitrobenzene and sodium methoxide the conditions should be such that substitution as far as possible precedes reduction, because *pp'*-dichloroazoxybenzene cannot easily be converted into *p*-azoxyanisole. Under the following conditions a yield of 64% of pure azoxyanisole is readily obtained.

69 C.c. of a methyl-alcoholic solution of sodium methoxide (containing 100 g. Na per litre) are boiled for 12 hours with *p*-chloronitrobenzene (31·5 g.), 51 c.c. of the methoxide solution are then added (total quantity, 50% in excess of the theoretical amount required to produce the azoxyanisole), methyl alcohol (50 c.c.) is distilled off, and the residue is boiled for a further 12 hours and then treated with hot water to dissolve the inorganic matter. Th

crude dry *p*-azoxyanisole obtained (23·5 g.) is recrystallised from boiling benzene (200 c.c.)-petroleum (130 c.c.; b. p. 80—100°), 14 g. of pure material being obtained directly and 2·5 g. from the mother-liquor by concentration to 150 c.c., dilution with petroleum (250 c.c.), and recrystallisation. The m. p. (118·5°) and the clearing point (134—135°) are unchanged by admixture of an authentic specimen of *p*-azoxyanisole.

Preparation of 3 : 3′-*Dichloro*-p-*azoxyanisole*.—1 : 2-Dichloro-4-nitrobenzene (m. p. 42°) is obtained in excellent yield after D.R.-P. 167297, but a chlorinating temperature of 95—105° and the presence of antimony trichloride (5% by weight of the *p*-chloronitrobenzene) are advantageous. It is converted into 3 : 3′-*dichloro*-p-*azoxyanisole* by using exactly the same molecular proportions of sodium methoxide and the other conditions recorded above. After crystallisation from benzene and from petroleum (b. p. 100—120°), the azoxyanisole is obtained in yellow prisms, m. p. 182° (yield, 10·5 g. from 19·2 g. of 1 : 2-dichloro-4-nitrobenzene). It does not form liquid crystals (Found: C, 51·3; H, 3·2. $C_{14}H_{12}O_3N_2Cl_2$ requires C, 51·4; H, 3·65%).—THE UNIVERSITY OF MELBOURNE. [*Received, February 1st,* 1929.]

The Action of Aromatic Acid Chlorides on Vinyldiacetoneamine.

By JOHN GRAYMORE.

IT has been shown by Kipping and Greasley (J., 1924, **125**, 2611) that vinyldiacetoneamine [2 : 2 : 6-trimethyl-4-piperidone] cannot be benzoylated by the Schotten–Baumann method: the only benzoyl derivative which is obtained is a trace of benzoic anhydride.

By heating vinyldiacetoneamine (2 mols.) with benzoyl chloride (1 mol.), however, they obtained a normal *N*-benzoyl derivative, $C_{15}H_{19}O_2N$, m. p. 156°, and when more benzoyl chloride was used an oil was produced from which ill-defined crystals of a structural isomeride, m. p. 110°, separated. Since further investigation was required in order to explain these observations, the author, at Professor Kipping's suggestion, has examined the behaviour of vinyldiacetoneamine towards various benzoylating agents.

Under the conditions of Schotten and Baumann acylation did not occur in any case, the results confirming those of Kipping and Greasley save that no anhydride formation took place. As this could be attributed to the presence either of water or of sodium hydroxide, experiments were made in aqueous solution in the absence of sodium hydroxide, but again no benzoyl derivative was formed, the benzoylating agent reacting to form a salt with the base, as the acid was precipitated on acidification.

With pure dry vinyldiacetoneamine (2 mols.) freshly distilled under reduced pressure, *m*- and *p*-nitrobenzoyl chlorides, *o*-nitro-*p*-toluoyl chloride, and *p*-toluenesulphonyl chloride (1 mol.) condensed in the cold in the expected manner to give normal *N*-acyl derivatives. The formation of isomerides was not observed and experiments with a larger proportion of the acid chloride were not made.

The yield in the case of *p*-nitrobenzoyl chloride was theoretical, but in all others not more than 75% of the calculated yield could be obtained. *N-m-Nitrobenzoylvinyldiacetoneamine* crystallises from hot acetone in long needles, m. p. 159—160°; it is insoluble in water and ether, very soluble in acetone, less so in chloroform, and fairly readily soluble in alcohol. The *p*-derivative crystallises from acetone in short needles, m. p. 170°. *N-o-Nitro-p-toluoylvinyldiacetoneamine*, m. p. 150—151°, and *N-p-toluenesulphonylvinyldiacetoneamine*, m. p. 184°, crystallise from alcohol.

A concentrated aqueous solution of ammonia and ethylamine react with benzoyl chloride in the expected manner; but in very dilute solution (less than 5%), where free ammonia and ethylamine molecules are few, the formation of benzoyl compounds takes place either not at all or on a greatly reduced scale. It seems probable, therefore, that vinyldiacetoneamine in aqueous solution combines with water to form the ammonium hydroxide, and that a hydrogen atom in such a quinquevalent ammonium group is not displaceable as is the case with certain hydrochlorides.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 6th*, 1928.]

Salicylaldehyde and its Methyl Ether. By MAURICE COPISAROW.

o-TOLYL carbonate, which is mentioned by Einhorn and Holland (*Annalen*, 1898, **301**, 115) and serves for the preparation of salicyl aldehyde by chlorination and subsequent hydrolysis (Raschig D.R.-P. 233631; Friedländer, "Fortschritte der Teerfarbenfabrik ation," vol. X, p. 163), was prepared by passing carbonyl chlorid into a solution of 108 g. of *o*-cresol and 42 g. of sodium hydroxid in 300 c.c. of water at 70—75° until the gas ceased to be absorbe The oily liquid that separated was triturated with cold dilut sodium hydroxide solution, washed, and dried. The white odourle product (yield, 100 g., *i.e.*, 83%) was chlorinated by Raschig method (*loc. cit.*): the reaction was accelerated by sunlight a was accompanied by the evolution of carbonyl chloride in additi to hydrogen chloride. *ωω-Dichloro-o-tolyl carbonate* was obtain as a thick brownish-yellow liquid which set to a translucent res and could not readily be purified.

The chlorination product (380 g.) from 1 g.-mol. of *o*-tolyl carbonate was suspended in 1200 c.c. of methyl alcohol, a solution of 260 g. of sodium hydroxide in 500 c.c. of water gradually added, and the mixture heated for 1 hour at 100°. The alcohol was then removed, and the residue acidified and steam-distilled. The pale yellow oil in the distillate was identified as salicylaldehyde (yield, 107 g.; 44%). The distillate contained 15 g. of dissolved salicylaldehyde (contaminated with salicylic acid), making the total yield of aldehyde 50%. Less satisfactory results were obtained by acid hydrolysis.

o-Anisaldehyde was prepared directly by the combined hydrolysis and methylation of the chlorination product. 120 G. of anhydrous sodium carbonate and 250 g. of methyl sulphate were gradually added to the hydrolysed chlorination product (before removal of the alcohol and acidification), the mixture was heated for 4 hours at 100°, the alcohol removed, and the residue acidified and distilled in steam. The product consisted of 103 g. (2% in solution) of anisaldehyde (yield, 38%) and 32 g. (6% in solution) of salicylaldehyde (yield, 13%). The anisaldehyde was ultimately obtained in small colourless crystals, m. p. 39—40°.

This method of preparing *o*-anisaldehyde is much more satisfactory than those already recorded (Perkin, *Annalen*, 1868, **145**, 302; J., 1889, **55**, 550; Voswinckel, *Ber.*, 1882, **15**, 2024; Irvine, J., 1901, **79**, 669; Katschalowsky and Kostanecki, *Ber.*, 1904, **37**, 2347).

The author is indebted to Mr. G. E. McKenlay, B.Sc. (Tech.), for his assistance in this work.—THE UNIVERSITY, MANCHESTER. [*Received, January 26th*, 1929.]

LXXXVI.—*The Alkalinity of Soap Solutions as measured by Indicators.*

By JAMES WILLIAM MCBAIN and KATHLEEN HAY.

THE classical experiments of Chevreul ("Recherches chimiques sur les corps gras d'origine animal," Paris, 1823) demonstrated clearly the existence of hydrolysis in aqueous solutions of sodium and potassium soaps, and gave some indication of the products of hydrolysis. Until recently, however, the extent of the hydrolysis was a matter of dispute and of wide divergence of opinion (see, *e.g.*, F. Goldschmidt, "Handbuch der Chemie und Technologie der Öle und Fette," Vol. III, 1911, pp. 405 and 411, where it is stated that this is "still an unsolved problem"). Contributions from the

Bristol Laboratory (McBain and Martin, J., 1914, **105**, 957; McBain and Bolam, J., 1918, **113**, 825; Beedle and Bolam, *J. Soc. Chem. Ind.*, 1921, **40**, 27 T; McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179; McBain and Jenkins, J., 1922, **121**, 2325; McBain and Bowden, J., 1923, **123**, 2417; M. E. Laing, *J. Physical Chem.*, 1924, **28**, 673; McBain and Buckingham, J., 1927, 2679) have established by many independent methods (hydrogen electrode, rate of catalysis, conductivity, ultrafiltration, and electric migration) that all aqueous solutions of the salts and acid salts of the fatty acids are definitely alkaline, although the concentration of hydroxyl ion is only of the order of $N/1000$ or less. Each of these methods has limitations, and the present contribution, in which the use of indicators is described, greatly extends the available data.

The investigation, which was completed at the University of Bristol in 1926, began by a study of the behaviour of all the commercially available indicators in alkaline solution in the absence of soap. Many surprising discrepancies were encountered,* including, for example, a very large salt error caused by the standard Sørensen buffers themselves with such indicators as thymol-blue, phenol-red, and phenolphthalein in alkaline solution. Some of th results of this study have been published by McBain, Dubois, an Hay (*J. Gen. Physiol.*, 1926, **9**, No. 4, 451). The work has bee supplemented and confirmed by the use of the hydrogen electrod by Miss Clark and Miss M. E. Laing at Stanford (*J. Gen. Physiol* in press).

Very few indicators possess any value for the study of soa solutions; for example, the Universal Indicator, which has bee used in several technical circles, yields completely erroneous result

The two best indicators are alizarin-yellow G (0·003—0·0005N–OE and phenolphthalein (0·0008—0·0001N–OH′). Thymol-blue agre with these (0·0007—0·0001N–OH′), though the colour changes a not so striking; *o*-cresolphthalein also gives the same results phenolphthalein if the correct concentration of indicator is us but phenol-red lies in a range of alkalinity so low (below 0·0001N–O as to be rarely suitable in soap solutions. The special techni employed to minimise or eliminate systematic error is to match colour given by indicators in standard Sørensen and Palitz buffers, glycine–sodium hydroxide and borax–boric acid, at with the same colour given by the indicator in solutions of sodium hydroxide at 20° and at 90°, and to use the hydr electrode in the dilute solutions of sodium hydroxide to cor

* (*Added to proof.*) Compare McCrumb and Kenny on the shortcomin the available indicators for alkaline solutions (*J. Ind. Eng. Chem.*, analy edition, 1929, **1**, 44).

for any effect of the indicators upon the hydroxyl-ion concentration. Thus colours given in the soap solutions at 20° and at 90° could be matched against these buffers at 20°, whilst the colours are directly interpreted in terms of true alkalinity at the temperature of the soap. Results obtained by this method agree with the best established results of the previous methods in the few cases where such comparison is possible.

Previous methods have given somewhat distorted results for soap solutions stronger than $N/10$ or $N/5$. In the *E.M.F.* method, the neglected diffusion potential, difficult to evaluate precisely, must render the apparent hydroxyl-ion concentration too great. On the other hand, it was shown by blank experiments that the catalytic method gave low results for concentrated soaps because of sorption of reacting substance by the soap. The truth lies between these two values, and the results with indicators fall in the expected place. This is seen from Table I, which gives the results for the two soaps for which data by these three methods are available.

TABLE I.

Concentration (N_w) * *of hydroxyl ion in soap solutions at* 90° *as given by indicators* (1), E.M.F. (2), *and catalysis* (3).

Sodium palmitate.

Conc. of soap.	$0{\cdot}042N_w$.	$0{\cdot}5N_w$.	$0{\cdot}8N_w$.
OH′ by (1)	0·0008	0·0010	—
OH′ by (2)	0·0010	0·0019	0·0022
OH′ by (3)	0·0009	0·0002	0·0002

Potassium palmitate.

Conc. of soap.	$0{\cdot}019N_w$.	$0{\cdot}042N_w$.	$0{\cdot}1N_w$.	$0{\cdot}3N_w$.	$0{\cdot}85N_w$.
OH′ by (1)	0·0010	0·0014	0·0016	0·0015	—
OH′ by (2)	0·0011	0·0010	0·00125	0·0019	0·0015
OH′ by (3)	0·0008	0·0009	0·0009	0·0006	0·0001

* A curiously arbitrary choice is inherent to the use of either the catalytic or the indicator method. This arises from the fact that concentrated soap solutions are so very much bulkier than the water they contain. For example, at 90° a $1{\cdot}0N_w$-solution of sodium palmitate contains only 1000 g. of water in 1328·0 c.c. of soap solution. When now, solutions of sodium hydroxide are found which exhibit the same rate of catalysis or the same colour of indicator as a given soap solution, does this mean that the amount of hydroxyl ions in the hydroxide is that which is producing the same effect in the same amount of water in the soap solution (N_w of OH′) or in the same total volume of soap solution (N_s of OH′)? In this paper it is called N_w. The difference is 32·8%, but this is proportional to the concentration and becomes inappreciable in dilute solution.

The hydrolysis alkalinity in the tables is reckoned on the total concentration of soap according to the formula:

$$\% \text{ Hydrolysis} = (N_w \text{ of OH}' \times 100)/(\text{Total } N_w \text{ of soap})$$

here N_w means equivalents per kg. of water.

Discussion.

The key to the understanding of the hydrolysis of soap solutions is the appreciation of the two factors: (*a*) that it is a property of the simple fatty ions, and (*b*) that it is due to the acid soap resulting from hydrolysis. Even the higher fatty acids are not particularly weak, and if it were not for the complexity and frequent insolubility of the acid soaps they would not be appreciably more alkaline than solutions of sodium acetate, which is hydrolysed only to the extent of 0·008% in 0·1*N*-solution at 25°.

The equation of hydrolysis, *viz.*, $P' + H_2O \rightleftharpoons HP + OH'$, refers directly only to the simple fatty ions; P represents a fatty radical such as palmitate, and HP the simple molecules of undissociated fatty acid. The concentrations of HP and of OH′ would be equal (and, like those in sodium acetate solution, almost negligibly small) were it not for the almost complete withdrawal from solution of the primary product of hydrolysis, the simple molecules of HP through formation of acid soap. This shifts the equilibrium as giver above to the right, with formation of a far higher concentration o hydroxyl ions:

$$HP + NaP \rightleftharpoons HP,NaP,$$

or, in some cases, $HP + 2NaP \rightleftharpoons HP,2NaP$.

The acid soap, HP,NaP, is formed so completely that there only the merest trace of free fatty acid left as such. This is co clusively shown by experiments on the equilibria in the presen of a second solvent such as benzene, toluene, or xylene. The lc concentration of the fatty acid in the non-aqueous layer, even wh the aqueous layer still contains more fatty equivalents of radic than of sodium, is thermodynamically conclusive proof that t aqueous layer is likewise unsaturated with free fatty acid. Th the aqueous layer of any pure or commercial soap, whether co taining excess, or even large deficiency, of sodium, never conta sufficient free fatty acid to saturate the water, in spite of the l solubility of these higher fatty acids. The concentration of hydro ion is of the order *N*/1000, and that of free fatty acid $10^{-6}N$, wher $10^{-5}N$ would be required for saturation. It is necessary to st these findings precisely, because they refute the opinions even a universally expressed in the literature, where it is taken for grar that free fatty acid occurs in soap solutions as free emulsified lic or suspended solid. The experimental evidence is summarise the communications of McBain, Laing, and Taylor (J., 1922, 1 621), McBain and Buckingham (*loc. cit.*), and McBain and E (J., 1928, 2166; see also, McBain and Stewart, J., 1927, 1!

The acid soaps are usually insoluble, but when sufficiently soluble they are colloidal electrolytes.

To sum up, the substance that hydrolyses is P′, the simple fatty ion; the hydrolysis is also conditioned by the locking up of the free fatty acid in the form of acid soap.

In sufficiently dilute solution (*e.g.*, less than $N/20$ at 90°), all soaps are simple crystalloidal salts like sodium acetate. Hence the degree of hydrolysis depends simply on the molecular weight; the higher the soap in the homologous series the greater the hydrolysis. Furthermore, potassium and sodium soaps are nearly identical. This is shown in Table II where also it is seen that in accordance with the greater solubility of the oleates as compared with stearates, the oleates are distinctly less hydrolysed. The oleates ($C_{\overline{18}}$, unsaturated) are very similar to palmitates (C_{16}, saturated); this is true for the sodium soaps in dilute solution up to $0{\cdot}02N$, and for the potassium soaps right up to $0{\cdot}4N$.

TABLE II.

Concentration of hydroxyl ion (N *of* OH′) *and hydrolysis* (%) *in* $0{\cdot}01N_w$-*soap solutions at* 90°.

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	0·00029N-OH′	2·9%	0·00025N-OH′	2·5%
Myristate, C_{14}	0·00033	3·3	0·00045	4·5
Palmitate, C_{16}	0·00074	7·4	0·00075	7·5
Oleate, $C_{\overline{18}}$	0·00081	8·1	0·00086	8·6
Stearate, C_{18}	0·0015	15·0	0·0013	13·0
Behenate, C_{22}	—	—	0·0029	29·0

In concentrated solutions the simple fatty ions P′ are largely eplaced by ionic micelles (P'_n) and hence there is less hydrolysis. Thus here it is the highest soaps that are least hydrolysed, and the ıydrolysis is less than in dilute solution, not merely relatively, but ıbsolutely. In other words, the hydroxyl-ion concentration ncreases as soap is gradually added to pure water, passes through a lat maximum and decreases again. The fact that in concentrated solution the highest soaps are less hydrolysed than the laurate (C_{12}) is shown in Table III.

TABLE III.

Concentration of hydroxyl ion (N *of* OH′) *and hydrolysis* (%) *in* $0{\cdot}5N_w$-*soap solutions at* 90°.

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	0·0034N-OH′	0·68%	0·0030N-OH′	0·6%
Myristate, C_{14}	0·00123 *	0·31	0·00092 *	0·23
Palmitate, C_{16}	0·0012	0·24	0·0010	0·2
Oleate, $C_{\overline{18}}$	0·0012 *	0·3	—	—
Stearate, C_{18}	0·0012 *	0·3	0·0010	0·2

* $0{\cdot}4N_w$-Soap.

The laurates (C_{12}) are crystalloidal up to much greater concentrations than the higher soaps, and hence not only develop a much higher hydroxyl-ion concentration but also do not reach a maximum value for the concentration of hydroxyl ions until in such concentrated soap solution as $0{\cdot}8N_w$. In contrast with this, the more colloidal palmitates (C_{16}) and oleates ($C_{18}^{=}$, unsaturated) attain maximum alkalinity between 0·07 and $0{\cdot}2N_w$. Sodium stearate (C_{18}) reaches its maximum alkalinity at $0{\cdot}05N_w$, whilst that of potassium stearate or sodium behenate (C_{22}) is practically constant from 0·02 to $0{\cdot}2N_w$. At room temperature, where the laurates are far more colloidal, they attain their maximum alkalinity at $0{\cdot}2N_w$ of soap; but the oleates have reached it at $0{\cdot}05N_w$. Th soaps of the higher, saturated, fatty acids are all too sparingl soluble to be investigated at 20°.

The change over from the increase of hydrolysis shown in Table I to the decrease shown in Table III is illustrated by the data fo $N/10$ soaps at 90° (Table IV), where six out of the ten soaps ar equally hydrolysed. In the more concentrated solutions th potassium soaps are very slightly more hydrolysed than the sodiu soaps.

TABLE IV.

Concentration of hydroxyl ion (N *of* OH′) *and hydrolysis* (%) *in* $0{\cdot}1N_w$*-soap solutions at* 90°.

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	$0{\cdot}00174N$-OH′	1·74%	$0{\cdot}0015N$-OH′	1·5%
Myristate, C_{14}	0·00123	1·23	0·00123	1·23
Palmitate, C_{16}	0·00172	1·72	0·0018	1·8
Oleate, $C_{18}^{=}$	0·00168	1·68	0·00094	0·94
Stearate, C_{18}	*0·00172*	*1·72*	*0·0011*	*1·1*

Table V shows how small is the absolute concentration of hydro: ions in extremely dilute solution, but how high a percentage hyd lysis this represents. Dilute solutions of a soap such as potassi laurate at room temperature are full of bulky crystalline sedim (acid soap), whereas a concentrated solution of the same soap the same temperature is as clear as water even in the ultramicrosc

TABLE V.

Concentration of hydroxyl ion (N *of* OH′) *and hydrolysis* (% *extremely dilute soap solutions* ($0{\cdot}0005N_w$) *at* 90°.

Na palmitate, C_{16}	0·00012—$0{\cdot}00007N$-OH′	24—1
Na oleate, $C_{18}^{=}$	0·00011	22
K palmitate, C_{16}	0·00018	36
K oleate, $C_{18}^{=}$	0·00011	22
K stearate, C_{18}	0·00038	76

The effect of temperature is slight in very dilute solution, although more pronounced in concentrated solution, but always in such a direction that hydrolysis is diminished on cooling provided that the soap stays in solution. Soap solutions from which soap has separated out on cooling (curded) are always distinctly more alkaline than the same system wholly in solution at, say, 90°. This accords with the observations of McBain and Martin (*loc. cit.*) with the hydrogen electrode; probably it is due to sorption of acid soap on the extensive surface of the freshly formed curd fibres. Equilibria are not attained here until after long periods. After 3 months, however, the alkalinity appears to be much the same as in the original solution at 90°.

Previous studies have shown that hydrolysis is not completely suppressed until excess of alkali to the extent of 3 or 4 equivalents per cent. has been added to a soap solution. Thereafter the alkalinity is just that of the added alkali. The slight amount of free alkali in a well-finished soap is of wholly negligible importance. Indeed, a small excess of alkali would, furthermore, be completely offset by the carbonic acid in ordinary tap-water. Addition of fatty acid decreases the alkalinity of a soap solution but never entirely removes it. Indicators confirm this. Owing to the insolubility of acid sodium palmitate, even at 90°, addition of palmitic acid renders a solution of sodium palmitate cloudy and heterogeneous.

EXPERIMENTAL.

The soap solutions were carefully prepared from Kahlbaum's purest fatty acid by the method of Bunbury and Martin (J., 1914, **105**, 417) after the molecular weight had been determined by dissolving the acid in freshly boiled-out, neutralised alcohol containing phenolphthalein and titrating it against the solution of sodium or potassium hydroxide which was to be used in making the soap.* It was arranged that in this titration the solution at the end-point contained 60—80% of alcohol. $N/5$- and $N/10$-Solutions were prepared and were diluted with freshly boiled-out conductivity water. The sodium hydroxide was carefully made, as described in previous communications, from drippings from metallic sodium free from carbon dioxide. Stoppered Jena-glass vessels were employed throughout. Solutions were prepared immediately before use by dilution of the drippings with freshly boiled-out conductivity water.

* This method of working must render negligible any influence of slight impurity in the fatty acid; specifically, the myristic acid was found to have slightly too high a molecular weight.

Two types of buffer mixture were used, Sørensen and Palitzsch's glycine–sodium hydroxide and borax–boric acid (Clark, "Determination of Hydrogen Ions," Wilkins and Williams, 1922). The glycine, sodium chloride, borax, and boric acid were Kahlbaum's purest. After addition of indicator, buffer solutions were kept *in closed vessels*; and to avoid error due to fading they were not kept more than 2, or sometimes 3, days. Tubes containing buffers with added phenolphthalein were sealed in an atmosphere of nitrogen free from carbon dioxide.

The amount of indicator added, as shown in the tables, was that required to produce maximum colour. The buffers contained 5 drops of 1% neutralised alcoholic solution of phenolphthalein in 20 c.c. of buffer solution. The colour of the solutions was matched by eye under a Sherringham Daylight Lamp in glass test-tubes of equal bore. Details of the standardisation of the colours given by buffers against known concentrations of pure alkali are recorded in previous references (McBain, Dubois, and Hay, *loc. cit.*; Clark and Laing, *loc. cit.*).

Experimental Data giving Hydrolysis Alkalinity (N_w of OH′) and Hydrolysis (%).

(Throughout these tables, the concentration of soap is given in terms of weight-normal, N_w, and the column headed "N_w-NaOH" shows the normality of the sodium hydroxide solution required to give a matching colour.)

Solutions of sodium laurate.

Conc. soap.	At 90°.* N_w-NaOH.	At 90°.* N_w-OH′.	At 90°.* %.	At 20°. N_w-NaOH.	At 20°. N_w-OH′.	At 20°. %.
0·5	0·003†	0·003	0·6	0·0011†	0·0010	0·2
0·2	0·0022†	0·0020	1·0	0·0012†	0·0011	0·55
0·1078	0·0017†	0·0016	1·5	0·0008†	0·0007	0·65
0·1078	0·00175‡	0·0016	1·5	0·0010‡	0·0009	0·8
0·1	0·0015†	0·0014	1·4	0·0010†	0·0009	0·9
0·05	0·00099†	0·00088	1·8	0·00075†	0·00066	1·3
0·05	0·00080§	0·00073	1·5	0·0008§	0·0007	1·4
0·02	0·00048‖	0·00043	2·15	0·00032‖	0·00027	1·35
0·02	0·00054§	0·00049	2·45	0·00032§	0·00027	1·35
0·01	0·00025‖	0·00021	2·1	0·00021‖	0·00017	1·7
0·005	0·00012‖	0·00008	1·6	0·00010‖	0·00007	1·4

* The sodium laurate used for solutions at 90° contained 1·8% equivalent excess of lauric acid.

† Indicator, 9 drops of 0·04% alizarin-yellow G.
‡ ,, , 10 drops of 0·04% alizarin-yellow G.
§ ,, , 10 drops of 1% phenolphthalein.
‖ ,, , 3 drops of 1% phenolphthalein.

Solutions of potassium laurate.

Conc. soap.	At 90°. N_w-NaOH.	N_w-OH′.	%.	At 20°. N_w-NaOH.	N_w-OH′.	%.
0·862	0·003†	0·003	0·35	0·0011†	0·0010	0·12
0·5	0·004†	0·004	0·80	0·0010†	0·0009	0·18
0·5	0·0028†	0·0026	0·52	0·0009†	0·0008	0·16
0·5	—	—	—	0·0008†	0·0007	0·14
0·3	0·0035†	0·0032	1·17	0·0008†	0·0007	0·23
0·2	0·0025†	0·0023	1·15	0·00107†	0·0010	0·50
0·1	0·00174†	0·0016	1·58	0·0008†	0·0009*	0·9
0·05	0·0012†	0·0011	2·2	0·0008†	0·0007	1·4
0·02	0·00036‡	0·00031	1·55	0·0003†	0·0002	1·0
0·02	—	—	—	0·0003§	0·00026	1·3
0·01	0·000285‡	0·00024	2·4	0·00023§	0·00019	1·9

Solutions of potassium laurate containing 0·07% *deficiency of alkali.*

0·5	0·0015†	0·0014	0·28	0·0004§	0·00036	0·07
0·4	0·00175†	0·00158	0·40	0·0004§	0·00036	0·09
0·294	0·00168†	0·00152	0·52	—	—	—
0·2	0·00168†	0·00152	0·76	—	—	—
0·1	0·0013†	0·0012	1·2	—	—	—
0·048	0·00082†	0·0007	1·5	0·00027§	0·00023	0·48
0·02	0·00023‡	0·00019	0·95	0·00022§	0·00018	0·9
0·01	0·00011‡	0·00008	0·8	0·00013§	0·00010	1·0

* Miss Laing determined the N_w-OH′ as 0·0011 by hydrogen electrode.
† Indicator, alizarin-yellow G.
‡ ,, , phenolphthalein.
§ ,, , 5 drops of 1% phenolphthalein.

Solutions of sodium and potassium myristate at 90°.

Conc. soap.	Sodium myristate. N_w-NaOH.	N_w-OH′.	%.	Potassium myristate. N_w-NaOH.	N_w-OH′.	%.
0·4	0·00092*	0·00091	0·23	0·00123*	0·00111	0·28
0·2	0·00123*	0·00111	0·56	0·00123*	0·00111	0·56
0·1	0·00123*	0·00111	0·11	0·00123*	0·00111	1·1
0·05	0·00123*	0·00111	2·2	0·00092*	0·00082	1·6
0·02	0·00083†	0·00077	3·85	0·00039§	0·00035	1·75
0·0195	—	—	—	0·00037§	0·00033	1·7
0·015	—	—	—	0·00035§	0·00031	2·1
0·01	0·00048†	0·00043	4·3	0·00033§	0·00029	2·9
0·005	—	—	—	0·00013§	0·00009	1·8
0·0001	0·00005‡	(0·00003)	(3·0)	—	—	—

* Indicator, 10 drops of 0·05% alizarin-yellow G.
† ,, , 10 drops of 1% phenolphthalein.
‡ ,, , phenol-red.
§ ,, , phenolphthalein.

Solutions of sodium and potassium palmitate at 90°.

Conc.	Sodium palmitate.			Potassium palmitate.		
soap.	N_w-NaOH.	N_w-OH′.	%.	N_w-NaOH.	N_w-OH′.	%.
0·5	0·0010*	0·0010	0·2	0·0012*	0·0010	0·20
0·4	0·00117†	0·0011	0·28	—	—	—
0·3	—	—	—	0·00168*	0·00152	0·51
0·25	0·0020*	0·0018	0·72	—	—	—
0·1	0·0018*	0·0016	1·6	0·00172*	0·00155	1·6
0·09	0·0018*	0·0016	1·6	—	—	—
0·05	0·00092*	0·00082	1·6	0·00172*	0·00155	3·1
0·024	—	—	—	0·00126*	0·00113	4·7
0·02	0·00092*	0·00082	4·1	—	—	—
0·01033	0·00076†	0·00070	6·8	—	—	—
0·01	0·00082†	0·00076	7·6	0·00074§	0·00067	6·7
0·0098	0·00068†	0·00062	6·2	0·0008*	0·0007	7·1
0·005	0·00046†	0·00040	8·0	—	—	—
0·0048	—	—	—	0·00054*	0·00047	9·8
0·002	0·00035†	0·00031	15·5	—	—	—
0·001	0·00019†	0·000158	15·8	0·000148§	0·000144	14·1
0·001	—	—	—	0·000144‖	0·000108	10·8
0·0005	0·00012‡	0·00009	18·0	—	—	—
0·0005	0·00007†	(0·00004)	(8·0)	—	—	—
0·00047	—	—	—	0·00013‖	0·00009	19·1

* Indicator, alizarin-yellow G.
† ,, , 5 drops of 1% phenolphthalein in 20 c.c. of solution.
‡ ,, , phenol-red.
§ ,, , thymol-blue.
‖ ,, , phenolphthalein.

Solutions of sodium and potassium stearate at 90°.

Conc.	Sodium stearate.			Potassium stearate.		
soap.	N_w-NaOH.	N_w-OH′.	%.	N_w-NaOH.	N_w-OH′.	%.
0·5	0·0010*	0·0010	0·2	—	—	—
0·4	—	—	—	0·0012*	0·0011	0·28
0·296	—	—	—	0·00168*	0·00152	0·51
0·2	0·0010*	0·0010	0·5	0·00168*	0·00152	0·76
0·1078	0·0017*	0·0015	1·4	—	—	—
0·1	0·0012*	0·0010	1·0	0·00172*	0·00155	1·55
0·1	0·0092*	0·00082	0·8	—	—	—
0·065	—	—	—	0·0018*	0·0016	2·5
0·05	0·0018*	0·0016	3·2	—	—	—
0·05	0·00107*	0·0010	2·0	0·0018*	0·0016	3·3
0·029	—	—	—	0·00168*	0·00152	5·2
0·02	0·0016*	0·0015	7·5	—	—	—
0·02	0·00123*	0·00111	5·6	—	—	—
0·015	—	—	—	0·00168*	0·00152	10·1
0·01	0·0014*	0·0013	13	—	—	—
0·01	0·00123*	0·00111	11·1	—	—	—
0·006	—	—	—	0·0013*	0·0012	20·0
0·005	<0·00099*	<0·0009	—	—	—	—
0·005	>0·00054†	>0·0005	—	—	—	—
0·003	—	—	—	0·0013*	0·0012	40
0·002	0·0008*	0·0007	35	—	—	—
0·0015	—	—	—	0·0011*	0·0010	66·6
0·0005	—	—	—	0·00038†	0·00034	68·0

* Indicator, alizarin-yellow G.
† ,, , phenolphthalein.

Solutions of the higher soaps at 20°.

Conc. soap.	N_w-NaOH.	N_w-OH′.	%.	Conc. soap.	N_w-NaOH.	N_w-OH′.	%.
	Sodium palmitate.				Sodium stearate.		
0·005	0·00040*	0·00030	(6·0)	0·005	0·00075*	0·00066	13·2
0·002	0·0008†	0·0007	35	0·002	0·0011*	0·00100	50·0
0·001	0·00031†	0·00027	27	0·002	0·00011†	0·00008	4·0
0·0005	0·00038†	0·00034	68	0·003	0·00025†	0·00021	7·0
	Potassium palmitate.				Potassium stearate.		
0·0098	0·0015*	0·0014	14·0	0·0005	0·00034†	0·00030	60·0
0·00047	0·00028†	0·00024	51·0				

* Indicator, alizarin-yellow G.
† ,, , phenolphthalein.

Solutions of sodium oleate at 90° and 20°.

Conc. soap.	At 90°. N_w-NaOH.	N_w-OH′.	%.	At 20°. N_w-NaOH.	N_w-OH′.	%.
0·3634	0·00038‡	0·00034	0·09	—	—	—
0·2	0·00092†	0·00082	0·41	—	—	—
0·1	0·00082†	0·00072	0·72	—	—	—
0·1	0·0012†	0·0010	1·0	—	—	—
0·1*	0·00080†	0·0007	0·7	0·00028§	0·00024	0·24
0·07	0·0012†	0·0010	1·4	—	—	—
0·05	0·0012†	0·0010	2·0	0·0009†	0·0008	1·6
0·02	0·00107†	0·0010	5·0	0·00062†	0·00054	2·7
0·01	0·00082§	0·00076	7·6	0·0012†	0·0010‖	10·0
				0·0009†	0·0008¶	8·0
0·01	0·00092†	0·00082	8·2	0·0005§	0·00045	4·5
0·005	—	—	—	0·00039‡	0·00034	6·8
0·0049	—	—	—	0·00035‡	0·00031	6·3
0·003	0·00038‡	0·00034	11·3	0·00036‡	0·00031	10·3
0·000286	0·00035‡	0·00031	10·8	—	—	—
0·00186	—	—	—	0·000345‡	0·00030	16·1
0·001	0·00029‡	0·00024	24·0	0·00029‡	0·00024	24
0·00097	0·000265‡	0·00023	23·7	0·000265‡	0·00023	24
0·0007	0·00165‡	0·00014	20	0·00024‡	0·00020	28
0·0005	0·00011‡	0·00008	16	0·00018‡	0·00014	28
0·00044	0·00011‡	0·0008	18	0·00015‡	0·00011	25
0·0003	—	—	—	0·00010‡	0·00007	23

* Solution prepared separately.
† Indicator, 10 drops of 0·05% alizarin-yellow G.
‡ ,, , 5 drops of 1% phenolphthalein.
§ ,, , 10 drops of 1% phenolphthalein.
‖ Before heating.
¶ After heating.

Solutions of potassium oleate at 90° and 20°.

Conc. soap.	At 90°. N_w-NaOH.	N_w-OH′.	%.	At 20°. N_w-NaOH.	N_w-OH′.	%.
0·413*	0·0012†	0·0011	0·27	0·000108†	0·000054	0·01
				0·00034‡	0·00030	0·08
0·2067	0·00168†	0·000152	0·735	0·00022†	0·00017	0·08
0·1018	0·00168†	0·00152	1·49	0·0003†	0·0002	0·20
0·0517	0·00168†	0·00152	2·94	0·0008†	0·0007	1·35
0·03995	0·00154†	0·00139	3·48	0·0007†	0·0006	1·5
0·0185	0·0012†	0·0011	5·95	0·0008†	0·0007	3·8
0·0102	0·0008†	0·0007	6·86	0·0003†	0·0002	2·0
0·00976	0·00082†	0·0007	7·2	0·0003†	0·0002	2·1
0·005088	0·00054†	0·00047	9·2	0·0003†	0·0002	3·9
0·0048	0·00054†	0·00047	9·8	0·0003†	0·0002	4·2
0·0031	0·00054†	0·00047	15·2	0·00022†	0·00017	5·5
0·001	0·0024‡	0·00020	20	0·000265‡	0·00023	23
0·001	0·00014‡	0·00010	10	—	—	—
0·0007	0·00015‡	0·00011	16	0·00024‡	0·00020	29
0·0005	0·00011‡	0·00008	16	0·00018‡	0·00014	28

* Prepared by Mr. Stewart; the other solutions were prepared by dilution from this.

† Indicator, 10 drops of 0·08% alizarin-yellow G.

‡ „ , 5 drops of 1% phenolphthalein.

*Solutions of sodium behenate at 90° and 20°.**

Conc. soap.	State of system.	N_w-NaOH.	N_w-OH′.	%.
0·2	90°, True jelly.	0·0073	0·0068	3·4
0·1	90°, „	0·0073	0·0068	6·8
0·05	90°, Viscous liquid.	0·0073	0·0068	13·6
0·02	90°	0·007	0·0065	32·5
	20°	0·010	0·009	45
0·01	90°, Almost clear liquid.	0·0029	0·0027	27
	20°, Milky liquid.	0·0073	0·0068	68

* Indicator, alizarin-yellow G.

*Solutions of sodium palmitate with added excess of palmitic acid.**

Conc. Na (N_w).	Conc. C_{16} (N_w).	Excess palmitate (%).	At 90°. N_w-NaOH.	N_w-OH′.	At 20°. N_w-NaOH.	N_w-OH′
0·4001	0·4001	0·00	0·00117	0·0011	—	—
	0·4041	1·00	0·000604	0·000549	—	—
	0·4201	5·0	0·000109	0·000073	—	—
	0·4669	16·7†	(0·00003)	(0·00003)	—	—
0·005	0·005	0·0	0·000458	0·0004	—	—
	0·00525	5·0	0·000417	0·000371	—	—
	0·00584	16·7	0·000376	0·00033	—	—
	0·00667	33·3	0·0003	0·00026	0·00031	0·00
	0·0075	50·0	0·0002	0·00016	0·00026	0·00
	0·010	100·0	0·000109	0·000073	0·00014	0·00
	0·0125	150·0	0·000077	0·000028	0·00059	0·00
0·01033	0·01033	0·0	0·00076	0·00070	—	—
	0·01085	5·0	0·000458	0·000412	0·0003	0·00
	0·01206	16·7	0·000376	0·00033	0·000198	0·00
	0·01377	33·3	0·000376	0·00033	—	—
	0·02066	100·0	0·000144	0·000108	0·0003	0·0(

* Indicator, 5 drops of 1% phenolphthalein in 20 c.c. of solution.

† Not homogeneous.

*Solutions of potassium oleate with added excess of oleic acid.**

Conc. K (N_w).	Conc. oleate (N_w).	Excess oleate (%).	At 90°. N_w-NaOH.	At 90°. N_w-OH′.	At 20°. N_w-NaOH.	At 20°. N_w-OH′.
0·04	0·04	0·0	0·00154	0·00139	0·0008	0·0007
0·0406	0·07267	78·98	0·00036	0·00031	0·0008	0·0007
0·025	0·025	0·0	0·00134	0·0012	0·00074	0·00068
0·02558	0·03887	50·00	0·00037	0·00033	0·00022	0·00018
0·0185	0·0185	0·0	0·0012	0·0011	0·0007	0·00069
0·01761†	0·02639	49·85	0·0008	0·0007	0·00035	0·00031
0·014	0·014	0·0	0·0010	0·0010	0·00045	0·00041
0·0139‡	0·0288	107·2	0·00033	0·00029	0·000115	0·00008

* Solutions prepared by Mr. Stewart. Indicators alizarin-yellow G, phenolphthalein.

† Cloudy. ‡ Very cloudy.

Summary.

1. Very few indicators are of any value for the study of the alkalinity of soap solutions, and even with them certain precautions must be observed. Determinations are recorded for solutions of pure potassium and sodium soaps at 20° and 90° over a wide range of concentration.

2. All the results harmonise with the recognition of two factors: (1) that hydrolysis is a property of the free, simple, fatty ion, not of any other ion, molecular species, or colloid; (2) that hydrolysis is chiefly due to the fatty acid formed being almost completely removed to form acid soap. Hence, all soap solutions are alkaline and none contains even the minute amount of free fatty acid required to saturate the water.

3. The results obtained support the conception that soap solutions are crystalloidal when sufficiently dilute, and colloidal in higher concentrations. For example, on the addition of soap to water the hydroxyl-ion concentration rises, passes through a flat maximum, and diminishes again as the soap solution becomes concentrated and the simple fatty ions are replaced by ionic micelles. The more colloidal the soap the sooner is the maximum hydrolysis alkalinity attained.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, November 16th,* 1928.]

LXXXVII.—*Constitutional Influences on the Conversion of Azonaphthols into their Azo-sulphites and their Bearing on the Structure of* α- *and* β-*Naphthol.*

By ALBERT THEODORE KING.

THE conversion of azonaphthols into their azo-sulphites is of special significance in the case of dyes derived from them, since this reaction underlies their degree of fastness to sulphur dioxide on alkaline

fabric as distinguished from the ordinary stoving test with excess of sulphur dioxide.

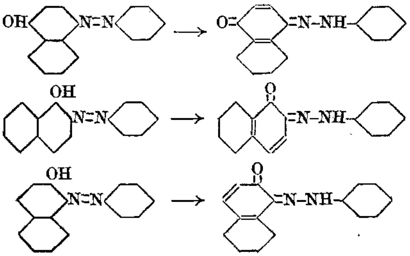
The indication previously made (King, J., 1927, 2639), that β-naphthol derivatives are more reactive to sodium bisulphite than α-naphthol derivatives, is supported by observations from the practical dyeing side by Goodall (*J. Soc. Dyers and Col.*, 1928, **44**, 145), who records that whereas all J. R. Geigy & Co.'s azo-dyes with β-naphthol residues proved to be sensitive to sulphur dioxide when tested over the "active range" of alkalinity on wool fabric, not one of the twenty α-naphthol derivatives tested was affected. This difference in activity is further considered in the present paper, more particularly with regard to the positional effect of sulphonic groups.

With the naphthol nucleus unsubstituted, the azo-α-naphthol bisulphite compounds form fairly readily, although less so than the corresponding β-naphthol compounds. For example, *p*-sulphobenzeneazo-α-naphthol reacts rather less readily than *p*-sulphobenzeneazo-β-naphthol, and 4-sulpho-α-naphthaleneazo-α-naphthol (Acid Brown R) distinctly less readily than the corresponding β-naphthol compound (Fast Red A). *No close comparison of constitutional influences can be drawn here, since the coupling of β-naphthol derivatives occurs at the ortho-position to the hydroxy-group, whereas with the above α-naphthol compounds the coupling is at the para-position to the hydroxy-group.*

When the naphthol component is sulphonated, however, so that the coupling is in the ortho-position for both α- and β-naphthol, a wide divergency in reactivity appears. The azo-β-naphthol-sulphonic acids show no falling off in reactivity; rather, owing to the increasing solubility accompanying introduction of sulphonic groups, conversion into the azo-sulphite becomes, if anything, more readily effected. The well-characterised sulphites of a number of azo-β-naphtholsulphonic acids are recorded in the experimental part. No example has so far been found where an azo-compound with a β-naphthol residue has failed to form a bisulphite derivative On the other hand, azo-derivatives of α-naphthol show a striking loss of reactivity with introduction of sulphonic groups, the only case of sulphite formation observed being with a sulphonic group in the 5-position and then only when the azo-derivative is formed from an unsulphonated diazo-compound. For instance, α-naphthaleneazo-α-naphthol-5-sulphonic acid (Double Ponceau) yields the azo-sulphite, but the corresponding 4-sulpho-α-naphthaleneazo-α-naphthol-5-sulphonic acid (Fast Red V.R.) merely undergoes slow fission, without any azo-sulphite formation occurring. The non-reactivity of the following dyes illustrates the general inhibitio

with a sulphonated α-naphthol component: α-naphthaleneazo-α-naphthol-4 : 8-disulphonic acid (Azo Bordeaux, Bayer), α-naphthaleneazo-α-naphthol-3 : 6-disulphonic acid (Benzyl Bordeaux B, Clayton Aniline Co.), 4-sulpho-α-naphthaleneazo-α-naphthol-4-sulphonic acid (Carmoisine, Sandoz), 4-sulpho-α-naphthaleneazo-α-naphthol-5-sulphonic acid (Fast Red V.R., Bayer), 6-sulpho-β-naphthaleneazo-α-naphthol-4-sulphonic acid (Brilliant Ponceau 4R, Bayer).

The mechanism of azo-sulphite formation has been well studied by Voroshcov (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 771; 1915, **47**, 1669), who regards the reaction as taking place by addition at the hydroxy-group in its ketonised form, in support of which view he discusses the relative activity of the three typical azo-linkings in their tautomeric forms as shown below:



He observed that compounds (I) and (III) react readily, whereas (II) is non-reactive, and regards this as additional evidence against Spiegel's view (*Ber.*, 1885, **18**, 1479), since if the reaction consisted in addition at the double bond, (II) would offer the least steric hindrance and react most readily, and (III) should react least readily. But "considering the action as jointly concerning the oxy-group, the most restrained oxy-group is in (II), which does not react, and this group in (I) and (III) is placed in equally reactive state."

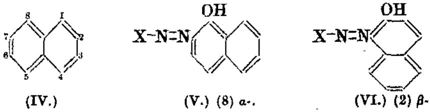
It would not seem, however, that any form of steric hindrance can play more than a minor part, in view of the marked reactivity of heavily substituted azo-β-naphthols, *e.g.*, 4-sulpho-α-naphthalene-azo-β-naphthol-3 : 6 : 8-trisulphonic acid, though the slowness of reaction with *m*-xyleneazo-β-naphthol-3 : 6-disulphonic acid (see experimental part) and also with *o*-carboxybenzeneazo-β-naphthol-3 : 6-disulphonic acid is probably a real steric hindrance effect.

Indeed the view that the naphthol nucleus reacts in a tautomeric keto-form involves the hypothesis that only those azonaphthols which are capable of assuming such tautomeric form can give rise to azo-sulphites, and the difference in behaviour appears to be due rather to some inherent disability of (II) to assume the tautomeric form necessary before any reaction can occur, whereas (I) and (III) can ketonise readily.

If this is so, Voroshcov's formulation above indicates in fact that (I) should be the least reactive, which point will be reverted to later, but there is no structural indication that tautomerisation should occur in (III) but not in (II) or that it would be prevented by substitution, even in adjacent positions.

On the other hand, the unsymmetrical form of the naphthalene ring would provide for a different behaviour, on the following reasoning, (1—2) in (IV) being regarded as a double-bond position. In the case of compound (II), with the hydroxy-group in position 1 tautomerisation involves no oscillation in the ring, only the swinging of the 1—2 double bond between the hydroxy-group and the 2-nitrogen linkage being required, as in the symmetrical formula. With the hydroxy-group in position 8, however, tautomerisation involves either a complete rearrangement of the double bonds to the symmetrical form, or a cyclic transformation round the whole nucleus into the alternative unsymmetrical formula. This is not absolutely precluded while the naphthol ring remains unsubstituted, but would tend to be blocked by substituents, especially in positions 5 and 6.

Applying the same reasoning to β-naphthols, if the hydroxy-group is in position 2, only the 1—2 bond oscillates, but if it is in position 7, the same complication obtains as in (8) α-naphthol. The contrast is portrayed by the formulæ for azo-α- (V) and -β-naphthol (VI) derivatives.



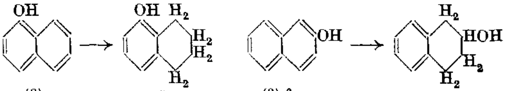
(IV.) (V.) (8) α-. (VI.) (2) β-.

Such a deduction would be very speculative on the single evidence of the contrast in reactivity of α- and β-naphtholazo-derivatives towards bisulphite, but the view that they are differently constituted, in that in the β-naphthol type the ring tends to stabilise with a double bond across the OH–N positions, and in the α-naphthol type with only a single bond, may have a bearing on the conflicting evidence regarding the constitution of azo-α- and -β-naphthols

and the well-known generally greater reactivity of the β-naphthol nucleus.

Further, similar configurations for α- and β-naphthol themselves would accord with certain contrasts in their behaviour, particularly their reduction by sodium and amyl alcohol to the tetrahydro-derivatives, α-naphthol giving almost solely *ar*-tetrahydro-α-naphthol, whereas β-naphthol gives mainly *ac*-tetrahydro-β-naphthol, accompanied by a relatively small quantity of the *ar*-derivative (Bamberger, *Ber.*, 1890, **23**, 197, 215, 888).

The symmetric and the centric formula do not suggest any directive influence in this reaction.



(8) α-. *ar*-. (2) β-. *ac*-.

But with the configurations above, the obvious product from α-naphthol is the *ar*-derivative, since a double bond between the α-position and the adjoining nucleus would be expected to be most resistant to reduction, which can only occur with accompanying rearrangement in the adjoining nucleus, or with the appearance of a double bond between the common carbon atoms.

The β-naphthol formula, on the other hand, clearly favours the formation of the *ac*-derivative, but as in this case the unsubstituted nucleus can oscillate between the unsymmetrical and the symmetrical configuration, the *ar*-derivative also can be produced.

That the initial reduction product from α-naphthol with sodium ud ethyl alcohol is the *p*-dihydro-α-naphthol (Rowe and Levin, ., 1921, **119**, 2021), whereas on either the above or the symmetrical formula an *o*-dihydro-derivative would be expected, is resumably accounted for by a bridge operating across the *p*-posiions (compare Ingold, J., 1922, **121**, 1133).

On hydrogenation under pressure, however, with a nickel catalyst, he *ac*-tetrahydro-derivative preponderates with α- as well as -naphthol (Brochet and Cornubert, *Bull. Soc. chim.*, 1922, **31**, 280), so that these conditions of reduction must over-ride any endency for the α-naphthol ring to be stabilised as postulated above.

Reverting to formula (I), it will be observed that the 1—4 posiions involve the same transposition to the para-quinonoid form whether the symmetrical or the unsymmetrical formula be employed, which is relatively simple, but less so than as formulated in (II) nd (III).

The 8—5 positions in the unsymmetrical form entail, not a

complete rearrangement as in the 8—7 position already discussed, but a more extensive one than the 1—4 positions require. The assumption of the 8—7 positions for the ortho-coupled α-naphthol would presumably determine the 8—5 positions for the para-coupling, and the observation recorded above, that benzeneazo-α-naphthol and α-naphthaleneazo-α-naphthol do form azo-sulphites but with definitely less readiness than the corresponding β-naphthol compounds, is at any rate in line with the 8—5 unsymmetrical structure.

With regard to the actual composition of the bisulphite compounds, the fission of the azo-linkage which usually occurs under prolonged treatment of azo-dyes of the α-naphthol type with bisulphite is of significance. Voroshcov, in his first paper, regarded the azo-sulphites as formed by loss of water from the intermediate additive product giving an azonaphthol sulphite similar to the naphthyl sulphites described by Bucherer (*J. pr. Chem.*, 1904, **69**, 49). He showed, however, in his second paper that Bucherer's products retain this molecule of water and he inclines to the same hydrated form for the azo-bisulphite compounds, which thus retain the hydrazone linking instead of reverting to the azo-linking, which would necessitate loss of the water molecule.

The analyses recorded in the experimental part are all lower than are required by the dehydrated form, but show generally a slightly higher content of SO_2 than is required for the hydrazone form. The difficulty both of purifying and of accurately analysing these compounds makes such evidence untrustworthy as to whether the water molecule is split off or not.

The marked difference in colour, however, between the dye and its bisulphite compound suggests a modified nitrogen linking, and this view is supported by the fact that the nitrogen link in the bisulphite product is stable to further action of bisulphite, whereas the azo-link is reduced.

Consequently, the bisulphite compounds are to be regarded as retaining the additive structure, without reversion to the azo linking by loss of water.

EXPERIMENTAL.

The azo-sulphites are in general readily obtained by stirring the powdered dye into excess of fairly concentrated sodium bisulphite solution, and warming the liquid at about 60° for an hour or so. The bisulphite solution is conveniently made by adding 10% sodium hydroxide solution to commercial bisulphite solution (20% SO_2) until the latter reacts only faintly acid to litmus paper, an approximately equal volume being required. The ease

isolating the azo-sulphite varies with the azo-compound employed. With the more difficultly soluble dyes it is preferable to use more dilute bisulphite solution, and addition of a little pyridine greatly facilitates the reaction. The hot liquid is filtered, and the filtrate cooled and saturated with sodium chloride. This in many cases causes the azo-sulphite to separate; it can then be purified by crystallisation first from 5% sodium chloride solution and finally from a small quantity of water.

Those azo-sulphites which are not capable of being salted out are most conveniently isolated by shaking the reaction mixture with pyridine (½ vol.) and adding sufficient sodium sulphate to cause ready separation of the pyridine layer. This contains the azo-sulphite, and is separated and well dried with anhydrous sodium sulphate. The filtered liquid is well stirred with ether (2—3 vols.), and the ether poured off, and this treatment is repeated. A third washing usually suffices for the ether to remain uncoloured, after which dry alcohol is stirred into the oily residue, which is more or less readily converted into a crystalline powder by rubbing. This is washed with dry alcohol and dried in a vacuum desiccator.

The compounds were analysed as previously described (J., 1927, 2644).

Sodium benzeneazo-6-sulpho-β-naphthyl sulphite (bisulphite compound of Croceine Orange, Bayer) separates readily from the cooled reaction mixture in flocculent form. After recrystallisation from warm water it dries to rather hard lumps which give a canary-yellow powder on rubbing (Found: S as sulphite, 7·2. $C_{16}H_{10}O_6N_2S_2Na_2,H_2O$ requires S, 7·05. $C_{16}H_{10}O_6N_2S_2Na_2$ requires S, 7·3%).

Sodium α-naphthaleneazo-6-sulpho-β-naphthyl sulphite (bisulphite compound of Fast Red B, Bayer). The dye is very slightly soluble in the bisulphite solution. The reaction is facilitated by addition of an equal volume of water and 5% of pyridine. The *azo-sulphite* is slowly salted out and gives a bronze-brown crystalline product on drying (Found: S as sulphite, 6·3. $C_{20}H_{12}O_6N_2S_2Na_2,H_2O$ requires S, 6·35. $C_{20}H_{12}O_6N_2S_2Na_2$ requires S, 6·6%).

Sodium 4-sulpho-α-naphthaleneazo-6-sulpho-β-naphthyl sulphite (bisulphite compound of Fast Red EA.S, British Dyestuffs Corpn.) separates readily on addition of sodium chloride and is purified by recrystallisation from dilute sodium chloride solution. The product on drying gives a bright orange crystalline powder (Found: S as sulphite, 5·2. $C_{20}H_{11}O_9N_2S_3Na_3,H_2O$ requires S, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3$ requires S, 5·4%).

Sodium benzeneazo-3 : 6-disulpho-β-naphthyl sulphite (bisulphite compound of Acid Orange R, British Dyestuffs Corpn.) is readily

salted out from the cooled bisulphite solution. Recrystallised from warm water, it yields a dull yellow crystalline powder (Found: S as sulphite, 5·8. $C_{16}H_9O_9N_2S_3Na_3,H_2O$ requires S, 5·75. $C_{16}H_9O_9N_2S_3Na_3$ requires S, 5·95%).

Sodium m-*xyleneazo-3 : 6-disulpho-β-naphthyl sulphite* (bisulphite compound of Ponceau 2RE, Geigy), in contrast with the other products described, forms only with difficulty, as already stated. Heating with dilute bisulphite solution and a little pyridine to 60° gradually brings the dye into solution, the latter eventually turning deep orange. The product, isolated by the pyridine method, is obtained as a buff yellow crystalline powder (Found: S as sulphite, 5·5. $C_{18}H_{13}O_9N_2S_3Na_3,H_2O$ requires S, 5·5. $C_{18}H_{13}O_9N_2S_3Na_3$ requires S, 5·65%).

Sodium o-*carboxybenzeneazo-3 : 6-disulpho-β-naphthyl sulphite* (bisulphite compound of Solochrome Red B, British Dyestuffs Corpn.) is obtained more readily in presence of pyridine. Isolation by means of the pyridine method gives a dull orange crystalline powder (Found: S as sulphite, 5·0. $C_{17}H_8O_{11}N_2S_3Na_4,H_2O$ requires S, 5·1. $C_{17}H_8O_{11}N_2S_3Na_4$ requires S, 5·3%).

Sodium α-naphthaleneazo-3 : 6-disulpho-β-naphthyl sulphite (bisulphite compound of Bordeaux B, Sandoz) also is obtained more readily in presence of pyridine. It is not salted out and is obtained from the pyridine extract as a brick-red crystalline powder (Found: S as sulphite, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3,H_2O$ requires S, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3$ requires S, 5·4%).

Sodium 4-sulpho-α-naphthaleneazo-3 : 6-disulpho-β-naphthyl sulphite (bisulphite compound of Azo Rubine S, Sandoz) is isolated from the pyridine extract as an orange-brown crystalline powder (Found: S as sulphite, 4·6. $C_{20}H_{10}O_{12}N_2S_4Na_4,H_2O$ requires S, 4·5. $C_{20}H_{10}O_{12}N_2S_4Na_4$ requires S, 4·6%).

Sodium 4-sulpho-α-naphthaleneazo-6 : 8-disulpho-β-naphthyl sulphite (bisulphite compound of Scarlet 5/O, British Dyestuffs Corpn.) is isolated from pyridine as a dull yellow crystalline powder (Found: S as sulphite, 4·6. $C_{20}H_{10}O_{12}N_2S_4Na_4,H_2O$ requires S, 4·5. $C_{20}H_{10}O_{12}N_2S_4Na_4$ requires S, 4·6%).

Sodium 4-sulpho-α-naphthaleneazo-3 : 6 : 8-trisulpho-β-naphthyl sulphite (bisulphite compound of Ponceau 6R, Bayer) is isolated from pyridine as a deep orange crystalline powder, deliquescing rapidly in air (Found: S as sulphite, 4·0. $C_{20}H_9O_{15}N_2S_5Na_5,H_2O$ requires S, 3·95. $C_{20}H_9O_{15}N_2S_5Na_5$ requires S, 4·0%).

Sodium α-naphthaleneazo-5-sulpho-α-naphthyl sulphite (bisulphite compound of Double Ponceau 2R, Bayer) is readily salted out from the reaction mixture and is obtained on recrystallisation from water as an orange crystalline powder (Found: S as sulphite, 6

$C_{20}H_{12}O_6N_2S_2Na_2,H_2O$ requires S, 6·35. $C_{20}H_{12}O_6N_2S_2Na_2$ requires S. 6·6%).

The author desires to express his thanks to Mr. E. W. M. Fawcett, of Keble College, Oxford, for his assistance in the preparation and analysis of a number of the azo-sulphites described.

British Research Association for the Woollen
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LXXXVIII.—*The Methylurethanes of the Isomeric α-Hydroxyphenylethyldimethylamines and their Miotic Activity.*

By Edgar Stedman and Ellen Stedman.

In investigations carried out by one of the authors during the past three years a new relationship between chemical constitution and physiological action has been discovered. It has been shown (*Biochem. J.*, 1926, **20**, 719; 1929, in the press) that certain urethanes possess in common, and to a more or less pronounced degree, the property of producing miosis when instilled into the eye. The effect of variations in the structure of the constituent portions of the molecule has not yet been completely determined, but it has been shown to be highly probable that miotic activity is only associated with urethanes which are phenyl, as distinguished from alkyl, esters of carbamic acids; that, of the substituted carbamic acids examined, the esters of methylcarbamic acid are, other conditions being the same, the most active miotics; and that the presence of a basic group in the molecule is essential for the activity of the urethanes.

The substances hitherto examined include two series of isomeric methylurethanes, namely, the dimethylaminophenyl esters of methylcarbamic acid, $NHMe\cdot CO\cdot O\cdot C_6H_4\cdot NMe_2$, and the methylurethanes of the hydroxybenzyldimethylamines,

$$NHMe\cdot CO\cdot O\cdot C_6H_4\cdot CH_2\cdot NMe_2.$$

None of the compounds of these series contains an asymmetric carbon atom, and, in view of the known difference in activity of the enantiomorphs of certain physiologically active substances, experiments have been carried out with the object of introducing such asymmetry into the latter of the above series of isomerides. For this purpose, the methylurethanes of the isomeric α-hydroxyphenylethyldimethylamines have been prepared, this particular series being chosen because the introduction of an asymmetric carbon

atom is effected with the minimal structural alterations necessary for this purpose. Unfortunately, despite numerous attempts, the authors have not yet succeeded in obtaining these urethanes in optically active forms. Work in this direction is still proceeding. In the meantime, the results obtained with the racemic bases are here recorded.

The preparation of the three isomeric urethanes was carried out in the following manner. The methoxybenzaldehydes were converted into the methoxyphenylmethylcarbinols by Grignard's reaction. By treatment with hydrobromic acid the carbinols yielded the corresponding bromides, which reacted with dimethylamine to give the α-methoxyphenylethyldimethylamines. These were demethylated with hydrobromic acid, and the phenols thus obtained converted into the methylurethanes, $NHMe{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CHMe{\cdot}NMe_2$, by interaction with methylcarbimide under appropriate conditions. The details of these reactions are described below and only the last stage need be commented upon here. Whereas α-*m*-hydroxyphenylethyldimethylamine reacts smoothly with an excess or the calculated quantity of methylcarbimide, with or without the use of an inert solvent, to yield the methylurethane, such is not the case with the *o*- and *p*-isomerides. If solutions of these substances in benzene are treated with an excess of methylcarbimide there results as product an oil from which no crystalline derivative can be prepared and which is clearly not homogeneous. By restricting the amount of methylcarbimide to one molecular proportion and carrying out the reaction in ethereal solution in the presence of a trace of the sodium salt of the phenol, formed by addition of a fragment of metallic sodium to the ethereal solution of the phenol, it has been possible to isolate the *o*-isomeride in a pure state. Identical conditions cannot, unfortunately, be employed for the preparation of the *p*-isomeride owing to the insolubility of the phenol in ether. If, in this case, benzene is employed as solvent in place of ether, the conditions being otherwise the same as those used for the *o*-isomeride, an oil is obtained which, although it is clearly not completely homogeneous, nevertheless yields a considerable proportion of the hydrochloride of the required urethane. Attempts to recover this urethane in a pure state from its hydrochloride, employing extremely mild conditions for the purpose, have failed. This failure may be connected with the instability of the urethanes. Instances are cited in the experimental section of decompositions which have occurred on the application of heat during the course of the preparation of the urethanes, and it has, in fact, been found advisable to carry out all stages of the preparation as far as possible at room temperature. [illegible]less, once the urethanes or their salts have been obtained

ı a solid state, they appear, as far as observation extends, to be uite stable in this condition at normal room temperature.

It was anticipated that the relative strengths as miotics of the ydrochlorides and methiodides of the methylurethanes of the omeric α-hydroxyphenylethyldimethylamines would correspond) those of the similar salts of the methylurethanes of the isomeric ydroxybenzyldimethylamines. This, however, has not proved › be the case. In the latter series (benzyl series) the activities of ıe hydrochlorides were in the order $o>p>m$; in the former -phenylethyl series) the order has been found to be $m>o, p$; ıd, just as in the benzyl series the *o*-compound was much more :tive than either the *p*- or the *m*-isomeride, so in the α-phenylethyl ries the *m*-compound has proved to be much more active than ıe *o*- and *p*-, the latter two isomerides being, in fact, only feebly :tive. In both series conversion of the tertiary bases into quatern·'y ammonium salts increased the miotic activity of the *o*- and iminished that of the *m*- and *p*-isomerides, the methiodides of the ·compounds being, indeed, inactive in the dilutions employed.

From the many examples which have now been brought forward, is clear that the physiological properties of urethanes of the 'pe discussed are due to the phenylcarbamate structure common to ıem all. The basic group, the presence of which is necessary ı other grounds, is also probably essential to the activity of the ›mpounds. In any case, variation in the nature of this group, ıch as the conversion of the tertiary base into a quaternary ammonım salt, or even a change in its position relative to the urethane :ouping, is seen to exert a profound influence on the activity of the ›mpounds. It is not proposed, however, to discuss the problem of ıe origin of these influences until further work on the pharmacogical action of these compounds, which has now been commenced, completed.

EXPERIMENTAL.

m-*Methoxyphenylmethylcarbinol*.—A solution of 60 g. of *m*-ethoxybenzaldehyde in an equal volume of dry ether was added ›wly to a solution of magnesium methyl iodide, prepared from ! g. of magnesium and 68 g. of methyl iodide, in 500 c.c. of dry her. The solution was then boiled under reflux for 30 minutes. n cooling, white crystals of the addition compound separated. ıe product was decomposed with hydrochloric acid and ice, and .e ethereal solution separated and dried over calcium chloride. vaporation of the ether yielded a straw-coloured liquid which ıs distilled under diminished pressure, *m*-methoxyphenylmethylrbinol being obtained in practically theoretical yield as a colourless scous liquid, b. p. 133°/14·5 mm.

α-m-*Methoxyphenylethyldimethylamine.*—A solution of the carbinol from the above experiment in 300 c.c. of benzene was saturated with dry hydrogen bromide. After the water formed in the reaction had been separated from the brown solution, the benzene and hydrogen bromide were removed by distillation under diminished pressure at a bath temperature not exceeding 35°. The crude α-*m*-methoxyphenylethyl bromide was dissolved in an equal volume of benzene, and the solution added slowly with gentle shaking to a solution of 50 g. of anhydrous dimethylamine in 250 c.c. of benzene cooled in a freezing mixture. After standing over-night, the solution was filtered from the dimethylamine hydrobromide which had separated, and extracted with hydrochloric acid. The acid extract was shaken with a small volume of ether to remove traces of benzene, and the base precipitated with sodium hydroxide and extracted with ether. After drying over sodium sulphate, the ether was removed and the residue distilled under diminished pressure.

α-*m*-Methoxyphenylethyldimethylamine is a colourless liquid, b. p. 118—119°/17 mm. (yield, 50 g.).

The hydrochloride is very soluble in alcohol, but is precipitated from the solution, by the slow addition of ether, in colourless prisms, m. p. 105° after softening at 101°.

The *methiodide* crystallises in flat, pale cream prisms, m. p. 142°, from alcohol, in which it is very soluble, on the addition of ether (Found: I, 39·4. $C_{12}H_{20}ONI$ requires I, 39·6%).

α-m-*Hydroxyphenylethyldimethylamine.*—A solution of the corresponding methoxy-compound (50 g.) in 200 c.c. of constant-boiling hydrobromic acid was boiled under reflux for 5 hours. After removal of the hydrobromic acid by distillation under diminished pressure, the residual syrup was dissolved in water, the solution made alkaline with sodium carbonate, and the precipitated oil extracted with ether. From the dried extract, an oil was obtained which rapidly crystallised (yield, 45 g.). When recrystallised by the slow addition of light petroleum to its solution in benzene, α-*m*-hydroxyphenylethyldimethylamine forms prisms, m. p. 87—88°. In the preparation of this phenol it is essential, if considerable losses are to be avoided, to boil the methoxy-compound with hydrobromic acid for a sufficient length of time to hydrolyse the methoxy-group completely, since a separation of the methoxy-compound from the phenol cannot be effected quantitatively by the customary methods. For instance, in an early experiment, an aqueous solution of the hydrobromide, prepared as described above, was made strongly alkaline with sodium hydroxide and then extracted with ether with a view to removing any unchanged methoxy-compound which might be present. On evaporation of the ether, however, th

residual oil crystallised and proved to be the required phenol, identical with a larger fraction obtained by extracting the mother-liquor, made alkaline with sodium carbonate. The acidic properties of this phenol are apparently so weak that its sodium salt is hydrolysed even in strongly alkaline solutions.

The *hydrochloride* crystallises from alcohol in colourless prisms, m. p. 197—198° (Found: Cl, 17·5. $C_{10}H_{15}ON,HCl$ requires Cl, 17·6%). The methiodide separates as micro-crystals, m. p. 160° after softening at 145°, from alcohol–ether.

α-o-*Methoxyphenylethyldimethylamine.*—*o*-Methoxyphenylmethylcarbinol was prepared from *o*-methoxybenzaldehyde (Baeyer and Villiger, *Ber.*, 1902, **35**, 3013) and magnesium methyl iodide. It was obtained as a thick oil, b. p. 128°/17 mm. (compare Pschorr and Einbeck, *Ber.*, 1905, **38**, 2077). This was treated successively with hydrobromic acid and dimethylamine under the same conditions as the *m*-isomeride. α-*o*-Methoxyphenylethyldimethylamine was thus obtained as a liquid, with a faint greenish-yellow colour, which, in two different experiments, had b. p. 105—107°/12 mm. and 108·5°/13·5 mm.

The hydrochloride was obtained as an oil which could not be crystallised. The *methiodide* separated from alcohol–ether in cream-coloured prisms, m. p. 136—137° (Found: I, 39·7. $C_{12}H_{20}ONI$ requires I, 39·6%).

α-o-*Hydroxyphenylethyldimethylamine.* — Hydrolysis of the methoxy-compound was effected as in the case of the *m*-isomeride. Conversion into the phenol was never, however, complete. It was therefore necessary to extract the product successively from solutions made alkaline with sodium hydroxide and with sodium carbonate. The extract from the former solution was a mixture of unchanged methoxy-compound and phenol, and that from the latter was practically pure phenol. On prolonged boiling with hydrobromic acid, considerable decomposition occurred in which dimethylamine was removed from the phenolic base. α-*o*-Hydroxyphenylethyldimethylamine is a colourless oil, b. p. 112—114°/14 mm.

The *hydrochloride*, m. p. 136—137°, crystallises on the slow addition of ether to its solution in alcohol (Found: Cl, 17·5. $C_{10}H_{15}ON,HCl$ requires Cl, 17·6%). An aqueous solution of this salt of the phenol gives an intense violet coloration with ferric chloride.

The reaction with methyl iodide yielded a sticky product from which, by crystallisation from alcohol, tetramethylammonium iodide was isolated. The methiodide is evidently unstable and decomposes with the elimination of the basic group.

p-*Methoxyphenylmethylcarbinol.*—This was prepared from anisaldehyde by the method employed for the *o*- and *m*-isomerides.

In the decomposition of the addition compound with magnesium methyl iodide care must be taken to prevent the solution from becoming acid, otherwise dehydration occurs with the formation of the corresponding styrene or its polymerisation products. For instance, in one experiment in which the carbinol was extracted from acid solution, an attempt was made to distil the product under diminished pressure. The boiling point rose slowly and continuously and the distillate became extremely viscid on standing. In a second similar experiment dehydration and polymerisation occurred even without distillation. In view of these results no further attempt has been made to distil this carbinol, but the crude product obtained by extracting the alkaline solution with ether has been employed for the following experiments without further purification.

α-*p*-Methoxyphenylethyldimethylamine, a colourless liquid, b. p 118°/14 mm., was prepared from the carbinol by the procedur adopted in the case of its isomerides (yield, 55·5 g. from 60 g. o anisaldehyde).

The *hydrochloride* crystallises from alcohol–ether in small prisms m. p. 213° (Found : Cl, 16·2. $C_{11}H_{17}ON,HCl$ requires Cl, 16·5%) The methiodide is readily soluble in alcohol, but separates fro alcohol–ether in plates, m. p. 128—130°.

Di-[α-p-*methoxyphenylethyl*]*dimethylammonium Bromide.*—Whe 57 g. of anhydrous dimethylamine were added to a benzene solutio of crude α-*p*-methoxyphenylethyl bromide, prepared from 60 of anisaldehyde, a vigorous reaction took place and a considerab amount of solid slowly separated. This was filtered off, treat with water to remove the dimethylamine hydrochloride, a crystallised from alcohol, *di*-[α-p-*methoxyphenylethyl*]*dimeth ammonium bromide* being obtained in thick plates, m. p. 10 (Found : loss on drying, 4·7. $C_{20}H_{28}O_2NBr,H_2O$ requires H_2 4·4%. Found in material dried in a vacuum: Br, 21· $C_{20}H_{28}O_2NBr$ requires Br, 20·3%). A further quantity separat as an oil, which slowly solidified, when the aqueous mother-liquor w made strongly alkaline with sodium hydroxide. The benz mother-liquor was worked up for α-*p*-methoxyphenylethyldimeth amine in the usual manner (yield, only 25 g.). The above quatern bromide was not formed when the α-methoxyphenylethyl brom was slowly added to a cooled solution of the dimethylamine benzene in the manner described in the preceding experiments.

α-p-*Hydroxyphenylethyldimethylamine.*—The product of hydrolysis of the methoxy-compound with hydrobromic acid obtained as a thick purple oil, from which the hydrobromide of phenolic base partly crystallised on cooling. The phenol libera

from this in the manner described for its isomerides was contaminated with a brown impurity which could not be completely removed by repeated crystallisations. The semi-crystalline mass was therefore ground with cold acetone, in which the hydrobromide is practically insoluble, and the residue washed thoroughly with acetone; an almost colourless, crystalline powder (64 g. from 55·5 g. of methoxy-base) was thus obtained. After recrystallisation from alcohol this was decomposed with sodium carbonate, and the phenolic base extracted with ether. α-*p*-Hydroxyphenylethyldimethylamine crystallises from benzene–light petroleum and has m. p. about 115° (not sharp).

The hydrobromide crystallises from alcohol, in which it is sparingly soluble, in long prisms, m. p. 178°. It is readily soluble in water and sparingly soluble in hot acetone. The *hydrochloride* crystallises from alcohol in rosettes of needles, m. p. 183° (Found: Cl, 17·7; N, 7·0. $C_{10}H_{15}ON,HCl$ requires Cl, 17·6; N, 6·9%). In aqueous solution it gives an intense violet coloration with ferric chloride. The methiodide could not be prepared. It apparently decomposes in a manner similar to its *o*-isomeride.

Methylurethane of α-m-Hydroxyphenylethyldimethylamine.—A solution of 4 g. of the phenol in 10 c.c. of benzene was treated with 2·1 c.c. (about 2 mols.) of methylcarbimide. On the following day the solvents were evaporated under diminished pressure, the residue was dissolved in ether, and the supersaturated solution of the urethane thus obtained rapidly filtered from a small quantity of brown material. The urethane partly crystallised from the filtrate and a further quantity was obtained on concentration of the ethereal solution (total yield, 3·6 g.). The *methylurethane* of α-*m*-hydroxyphenylethyldimethylamine is moderately easily soluble in benzene, although it can be crystallised from this solvent, and insoluble in light petroleum. It is best crystallised from ether, from which it separates as tablets with triangular ends, m. p. 86° (Found: N, 13·0. $C_{12}H_{18}O_2N_2$ requires N, 12·6%).

The hydrochloride was prepared from the base and hydrogen chloride in cold alcohol, and separated on the addition of dry ether. It is very soluble in alcohol, insoluble in acetone, and separates from alcohol–ether in rosettes of prisms which melt incompletely and with effervescence at 169°. In the preparation of this hydrochloride it appears essential to use cold reagents. On one occasion the solid base was warmed with alcoholic hydrogen chloride on the water-bath to hasten solution: addition of ether precipitated an oil which would not crystallise. It is probable that warming caused partial hydrolysis of the urethane group with the consequent formation of a mixture of products.

When methyl iodide is added to a solution of the base in acetone, the *methiodide* separates slowly as an oil which slowly crystallises—a process which is accelerated by seeding. When ether is added to an alcoholic solution of the methiodide, this again separates as an oil which only crystallises after some hours. It then has m. p. about 130° (effervescence and after previous sintering) and is quite pure (Found : I, 34·8. $C_{13}H_{21}O_2N_2I$ requires I, 34·9%).

Methylurethane of α-o-*Hydroxyphenylethyldimethylamine.*—After a number of experiments carried out in benzene solution, from which no homogeneous product could be isolated, this urethane was finally obtained under the following conditions. A trace of metallic sodium was added to a solution of 1 g. of the phenol in 5 c.c. of ether. The sodium dissolved with the evolution of hydrogen. Methylcarbimide (0·48 c.c.; 1 mol.) was then added, and the mixture allowed to stand. After 2 days, large crystals of the urethane separated. The supernatant liquid was decanted and the crystals were washed with a small volume of ether, dissolved in warm benzene, and filtered from a small quantity of flocculent material; the urethane then separated in prisms, m. p. 90°. Addition of light petroleum to the benzene solution caused the separation of a further quantity of the urethane. The ethereal mother-liquor from the above preparation was evaporated under diminished pressure at room temperature; the oily residue slowly crystallised. The crystals were dissolved in a small volume of ether, but on evaporation of the latter on a water-bath the residue failed to crystallise, apparently owing to partial decomposition of the urethane during the evaporation.

The hydrochloride separates in crystalline form from alcohol-ether, but is so extremely hygroscopic that it is transformed into a pasty mass during the short time necessary for filtration. The *methiodide* separates from a solution of the base and methyl iodide in acetone on the addition of ether. When recrystallised from acetone, it forms prisms, m. p. 148° (efferv.) (Found : I, 34·3. $C_{13}H_{21}O_2N_2I$ requires I, 34·9%).

Methylurethane of α-p-*Hydroxyphenylethyldimethylamine.*—Attempts to prepare this urethane in the free state have not been successful. Of six experiments carried out under various conditions, the following gave the best result. A trace of sodium was added to a solution of 2 g. of the phenol in 15 c.c. of benzene. When this had dissolved, 1 c.c. of methylcarbimide was added, the solution being kept cool in ice. After 2 days, a small quantity of amorphous material was removed by filtration and the solvents were evaporated under diminished pressure at low temperature. The oily residue, which showed no signs of crystallising even after

ome days, was dissolved in ether and treated with alcoholic hydrogen hloride; the *hydrochloride* of the required urethane then separated s a sticky mass which became solid on the addition of further lcohol and rubbing (yield, 1·4 g.). It was recrystallised from lcohol and had m. p. 203° after previously sintering (Found: N, 10·9. $C_{12}H_{18}O_2N_2$,HCl requires N, 10·8%). In an attempt to ecover the urethane a suspension of the hydrochloride (0·5 g.) in ther was treated with 40 c.c. of *N*/10-sodium carbonate, and the ase extracted with ether. Evaporation of the dried ethereal xtract at low temperature left a thick oil which would not crystallise. Its solution in acetone was therefore treated with methyl odide; the *methiodide* separated as an oil which subsequently rystallised. Recrystallised from alcohol, it formed plates, m. p. 73° (efferv.) (Found: I, 35·2. $C_{13}H_{21}O_2N_2I$ requires I, 34·9%).

Miotic Action of Urethanes.—The three urethanes have been ested for miotic activity in the form both of their hydrochlorides nd methiodides by instillation into cats' eyes. For this purpose ·5% solutions of the substances in physiological saline have, in eneral, been employed. In the case of the hydrochloride of the nethylurethane of α-*o*-hydroxyphenylethyldimethylamine, which s extremely hygroscopic, the free urethane was dissolved in the alculated quantity of 0·153*N*-hydrochloric acid and then diluted to ·5% with physiological saline. With the exception of the nethiodide of the methylurethane of α-*p*-hydroxyphenylethyl-limethylamine, which had no action at this dilution, a contraction f the pupil resulted in each case, the extent of the miosis differing vith the various substances employed. The estimated order of ctivity is: *m*-HCl>*o*-MeI>*p*-HCl, *o*-HCl, *m*-MeI>*p*-MeI. This rder can, of course, only be regarded as a provisional one until the ctivities on other organs have been compared. Nevertheless it hould be pointed out that the observed activities of *p*-HCl, *o*-HCl, nd *m*-MeI were, in the dilutions employed, quite small, those of he *m*-HCl and *o*-MeI being very much greater. In the case of the *n*-HCl the action was extremely intense and persisted for a period xceeding 18 hours. It is probable that the miotic activity of this ubstance approaches, if not equals, that of physostigmine.

The expenses of this investigation, which has been carried out luring the tenure by one of us of a Carnegie Teaching Fellowship, ave been partly met by grants from the Moray Research Fund of his University.

DEPARTMENT OF MEDICAL CHEMISTRY,
UNIVERSITY OF EDINBURGH. [*Received, December 13th*, 1928.]

LXXXIX.—*Colloidal Platinum. Part V. The Coagulation by Electrolytes in Acid Solution.*

By Stuart W. Pennycuick.

The coagulation of colloidal platinum in acid solution differs in some essential characteristics from that in basic solution. The latter is dealt with in the next communication.

The *natural acidity* of platinum sols and their coagulation by various acids have already been discussed (J., 1928, 551). The experiments with hydrochloric and nitric acids as coagulants were repeated, the coagulated (frozen) solution being used as comparison solution. The more exact results led to the same conclusion, namely, that during coagulation none of the added acid is removed by the coagulum. The interpretation of the acid coagulation as being due to a depression of ionisation of a strong acid, probably $H_2Pt(OH)_6$ (see J., 1928, 2018), which occurs in considerable amount on the surface, is in keeping with the theory of colloid structure and surface ionisation, as developed by Pauli (see, *e.g.*, *Kolloid Z.*, 1926, **38**, 22; "Eiweisskörper und Kolloide," J. Springer, Wien, 1926; Pauli and Valkó, *Z. physikal. Chem.*, 1926, **121**, 161).

Ionic Exchange at the Colloid Surface.—It has been shown by Pauli and co-workers (*loc. cit.*) that, for such colloids as ferric hydroxide, aluminium hydroxide, and arsenious sulphide, only a fraction of the stabilising surface ionogen is actually ionised, or, in terms of the modern electrolyte theory as applied to colloids (Bjerrum, *Z. physikal. Chem.*, 1924, **110**, 756; Pauli and Valkó, *loc. cit.*), that the activity of the colloid ion is less than unity. It is also shown (*e.g.*, Pauli and Schmidt, *Z. physikal. Chem.*, 1927, **129**, 199) that on the addition of a foreign electrolyte there is an ionic exchange at the colloid surface, and that this precedes, and leads to, coagulation. Achar and Usher (J., 1927, 1875) have also shown that the addition of a neutral salt to a suspension of stearic acid produces free acid, due to a kationic surface exchange.

Now it is doubtless true that the hexahydroxyplatinic acid at the surface of the colloidal platinum particle is also only partly ionised, and in keeping with the above, the addition of a salt should cause a kationic interchange at the surface, with the liberation of acid. It is important to the general behaviour of platinum sols to show whether such a change does or does not take place.

Experimental.

Owing to the very low concentration of the colloid the choice of methods is limited, but the conductivity method appeared to be

most capable of accurately detecting any such change. Details concerning the conductivity cells used, and also the preparation of the pure platinum sols, are set out in previous papers. In the presence of salts, conductivity measurements do not give a direct indication of the hydrogen-ion concentration. Accordingly recourse was had to a comparative method which proved very satisfactory. One litre of the platinum sol was prepared, and boiled for 30 minutes. The preparation was then divided into halves, and one half was frozen, the colloidal platinum being thereby completely removed. On reboiling the coagulated (frozen) sol for 2 minutes, one obtained a conductivity a little greater than that of the original platinum sol. This could be diminished as required by dilution. Two comparison solutions were thus obtained: one contained the colloidal platinum with its usual environment of free hexahydroxy-acid, and the other contained exactly the same environment but no colloid particles. By using these solutions side by side, one can detect the changes due to the colloid particles themselves.

A weighed sample of the platinum sol (about 34 g.) was introduced into the conductivity cell and placed in the thermostat at 25° until its conductivity reached a steady value. The salt solution (*e.g.*, silver nitrate) was then added from a 5 c.c. burette till the coagulation point was passed, and the conductivity–concentration curve was drawn. All the precautions previously outlined were observed. The experiment was repeated with the coagulated (frozen) solution of the same initial conductivity.

TABLE I.

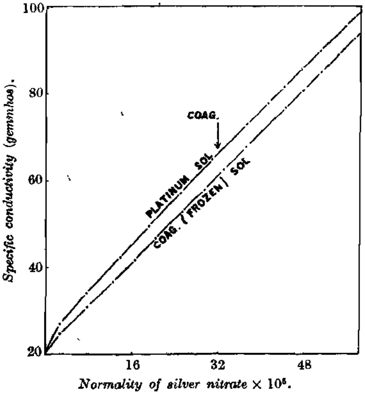
Volume of solution initially in cell, 35 c.c. Normality of added $AgNO_3$, 0·002*N*.

Platinum sol.				Coagulated (frozen) sol.			
$AgNO_3$ conc. $\times 10^5$.	κ.	$AgNO_3$ conc. $\times 10^5$.	κ.	$AgNO_3$ conc. $\times 10^5$.	κ.	$AgNO_3$ conc. $\times 10^5$.	κ.
—	20·19	41·38	77·73	—	20·23	33·12	62·62
2·70	26·55	44·40	81·47	2·71	24·70	37·26	67·72
7·58	33·98	47·64	85·69	7·59	30·90	41·07	72·83
13·67	42·25	51·01	89·86	12·34	36·78	44·52	76·64
19·10	49·37	55·67	95·43	16·29	41·78	47·87	80·83
25·01	57·01	58·09	98·37	20·06	46·54	51·35	84·98
30·85	64·77	60·05	100·58	25·09	52·55	54·53	88·88
37·28	72·74	—	—	29·32	57·95	57·37	92·30

It will be convenient to discuss one set of curves at once, and the data for the silver nitrate titrations are accordingly set out in Table I, and the corresponding curves in Fig. 1. From these it is seen that the addition of silver nitrate to the platinum sol always

results in a larger conductivity than the corresponding addition to the coagulated (frozen) sol. The explanation of this increased conductivity must be in terms of the liberation of an ion of greater mobility, and one must therefore conclude that some of the hydrogen ions at the surface of the colloid and an equivalent amount of silver ions from solution have exchanged places. The maximum divergence in the curves is seen to be of the order of 5 gemmhos, and on the assumption that this is wholly due to the kationic interchange, the concentration of silver ion so removed (or of hydrogen ion set free) is written as 5/(349,500—63,400), *i.e.*, 0·000017*N*. (The mobilities

FIG. 1.



of the hydrogen ion and the silver ion at 25° are taken as 349·5 an(63·4 respectively.)

Salts with Univalent Kations.—With potassium nitrate and sodium chloride, the exact divergence in the curves was difficult to obtain This was not unexpected. The coagulation concentrations of such salts are of the order 0·004*N* (compare 0·0003*N* for silver nitrate) and accordingly their curves have to be carried to such high con ductivities that the relatively small differences sought are les accurately picked out. With these salts, however, positive evidenc of the interchange was forthcoming.

Salts with Bivalent Kations.—Barium chloride, calcium nitrate and copper sulphate, all of which have relatively low coagulatio

concentrations (approx. $0{\cdot}0002N$), show the same sort of divergence as that outlined for silver nitrate. The maximum divergence was somewhat smaller, and lay between 2·5 and 4·0 gemmhos.

Salts with Tervalent Kations.—Aluminium sulphate and aluminium chloride gave corresponding results, but ferric chloride was anomalous (see later). The curves for aluminium sulphate are particularly interesting: they showed a maximum divergence (coagulation concentration $0{\cdot}000024N$) of 4 gemmhos, and since they presented no anomalies, the foregoing general interpretation holds. Now Burton (*Phil. Mag.*, 1906, **12**, 472) has calculated the charge on colloidal silver particles on the assumption that, on coagulation with aluminium sulphate, the whole of the salt is adsorbed. The calculation is assumed to be applicable to any colloidal metal. The reason for the extremely high values obtained is now evident. The relative positions of the curves for colloidal platinum show that the whole of the aluminium sulphate is not adsorbed, nor, in keeping with the general results, is there any evidence that any of the salt is adsorbed.

The Coagulation Process.—Bjerrum (*loc. cit.*) and Pauli and Valkó (*loc. cit.*) have shown that the modern theory of strong electrolytes is capable of extension to colloid solutions. Every colloid particle is an ion of high valency with a definite activity. The corresponding "gegenion" or colloid contra-ion will also have its own activity. Any increase of the latter will result in a decrease in the activity of the colloid ion. When this activity tends towards zero, *i.e.*, when the charge on the colloid tends to disappear, the colloid becomes unstable and coagulation ensues. As colloidal platinum is an acid sol containing the hydrogen ion as the contra-ion, the explanation of the coagulation by different acids at a fixed p_H follows.

The foregoing experimental evidence shows that on addition of a alt, *e.g.*, silver nitrate, there is always a kationic interchange, and hat some of the surface hexahydroxy-acid is converted into the orresponding silver salt. Any further increase in the silver itrate concentration not only produces more of the surface silver alt, but decreases the activity of the corresponding colloid ion. At definite silver-ion concentration, the latter activity has been ufficiently decreased to allow coagulation to ensue. This xplanation appears to be perfectly general.

The well-known increase in coagulating power of different alts with increase in the valency of the coagulating ion is explained n terms of the increase in the attractive force between the higher-valency ion and the colloid ion. All bivalent kations are accordingly tronger coagulants than univalent, and all tervalent stronger than ivalent.

Ions of the same valency have not exactly the same coagulating power, and here the effect of the atomic volume of the ion and other specific properties come into question. In this connexion one might notice that the silver ion, of low atomic volume, has a high coagulating power, not only towards platinum, but to all negative sols.

Partial Kationic Interchange.—Ferric chloride exhibits some peculiarities which can be directly explained. The curves obtained by adding this salt to the platinum sol and to the coagulated (frozen) sol do not show a deviation comparable with that for aluminium sulphate; in fact, the maximum deviation is only about 1 gemmho. Now the author has measured the hydrolysis of these two salts at the low concentrations employed, and whilst the aluminium sulphate is hydrolysed to the extent of about 35%, ferric chloride shows over 90% hydrolysis. Coagulations with the latter solution are then largely acid coagulations, where the ferric ion (owing to its extremely low concentration) plays perhaps a secondary part. The coagulation concentrations concerned support this view. The less hydrolysed aluminium sulphate coagulates at 0·000024*N*, whereas for the highly hydrolysed ferric chloride the corresponding concentration is 0·0001*N*. The latter value is much closer to the coagulating value for either hydrochloric or sulphuric acid, *viz.*, 0·0002*N*.

It is now clear why the ferric chloride addition curves show such a small deviation. (The pure acid sols show no deviation whatsoever.) These results further directly indicate that the ferric hydroxide of hydrolysis takes no appreciable part in the coagulation.

All the solutions concerned in the foregoing work are acid solution of low concentration, the acid being the free hexahydroxy-acid Now the kationic interchange will be subject to (but not necessaril solely controlled by) the law of mass action, and the question the arises whether all such salt coagulations are not mixed coagu ations of acid and salt, ferric chloride being a rather extreme case In all probability this is so, and the coagulum contains some of th original surface acid as well as the newly formed surface sal Herein lies the explanation of the decrease in the coagulation co centration of any salt as the sol is made more acid. A quantitati study over the possible acid range is incomplete, but the followi figures illustrate the effect of increasing the acid content :

	For 0·00005*N*-$H_2Pt(OH)_6$ (free).	For same with addition of 0·000102*N*-HNO_3.
Coag. conc. of NaCl	0·004*N*	0·0018*N*
,, ,, $AgNO_3$ ...	0·0003*N*	0·00015*N*
,, ,, $BaCl_2$ ...	0·0002*N*	0·00012*N*
,, ,, $FeCl_3$ ...	0·0001*N*	0·00007*N*

It is evident that coagulation concentrations have no definite significance unless the p_H of the solution is stated.

In neutral solutions the coagulation concentrations are slightly greater than those in the pure (naturally acid) platinum sol. For these measurements sodium or potassium hydroxide must be used as neutralising agent, for the salts of these bases with the free platinic acid are poor coagulants, and therefore introduce a minimum of complications. One must be careful not to pass the neutralisation point in such solutions, for the free hydroxides have far-reaching influences (see following paper).

Summary.

Experimental evidence is produced which shows that, on the addition of salts to colloidal platinum sols, the kation of the salt replaces the hydrogen ion of the surface hexahydroxy-acid. This kationic interchange precedes, and in fact directly leads to, coagulation. The coagulation process is discussed.

In acid solutions the kationic interchange is only partial and the coagulum contains some of the surface acid. This is shown to explain the increase in the coagulation power of a salt as the p_H of the sol is decreased.

It is also shown that with ferric chloride and aluminium sulphate, at the usual low concentrations, the hydroxides set free by hydrolysis play no important part in the coagulation.

UNIVERSITY OF ADELAIDE, AUSTRALIA.
UNIVERSITY OF CALIFORNIA,
BERKELEY. [*Received, November 6th,* 1928.]

XC.—*Colloidal Platinum. Part VI. The Behaviour of Platinum Sols in Basic Solution.*

By STUART W. PENNYCUICK.

(1) *The Action of Bases at the Colloid Surface.*

BEFORE the coagulation in basic solutions can be discussed, it is necessary to establish the part played by bases alone.

Any well-prepared sample of colloidal platinum is continually undergoing constitutional changes. This is shown by the steady increase in conductivity of the sol, as measured over several days (see J., 1928, 551). These changes demand that, where strict comparisons are to be made, either the same solution or strictly comparable solutions must be used. This condition is observed throughout the following work.

The Neutralisation of the Surface Hexahydroxy-acid.—If the platinum sol is titrated with barium and with sodium hydroxide, curves D and B respectively are obtained (see Fig. 1A; also J., 1928, 2111), although when the coagulated (frozen) sol is titrated with the same two bases, the corresponding curves are almost coincident and may be represented by curve C (which is actually that relating to barium hydroxide). This fundamental difference between the action of the two bases needs explanation.

The difference in concentration at the points B and C (*viz.*, $1 \cdot 6 \times 10^{-5}$ equiv.) represents the amount of sodium hydroxide removec by the colloid particles. In keeping with the results already recorded, this removal is interpreted as due to the neutralisatio of the surface acid, probably $H_2Pt(OH)_6$, with the formation of th corresponding surface salt. One may conclude then, that the tot surface acid, ionised and un-ionised, corresponds to $1 \cdot 6 \times 10$ equiv.

In the same way, the difference in concentration at the points and C represents the amount of barium hydroxide removed b the colloid particles. This is read from the curves as $6 \cdot 7 \times 10$ equiv. Of this, only $1 \cdot 6 \times 10^{-5}$ equiv. is needed to neutralise t surface acid, and the remainder must therefore be taken up by t surface in some other manner. Further evidence in this directi is provided by the back titration of the removed barium hydroxic

TABLE I.

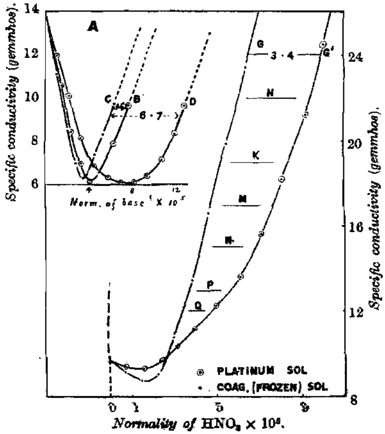
Titration and Back-titration.

Platinum sol.				Coagulated (frozen) sol.			
Titration.		Back-titration.		Titration.		Back-titration.	
Normality $Ba(OH)_2 \times 10^5$.	κ.	Normality $HNO_3 \times 10^5$.	κ.	Normality $Ba(OH)_2 \times 10^5$.	κ.	Normality $HNO_3 \times 10^5$.	κ.
—	13·92	—	9·66	—	13·88	—	9·
1·02	11·98	0·78	9·36	1·05	11·10	0·67	9·
2·09	10·07	1·58	9·29	2·15	8·42	1·45	8·
3·28	8·14	2·40	9·70	2·78	6·91	2·22	9·
4·47	6·82	3·18	10·37	3·34	6·16	2·98	10
5·81	6·15	3·97	11·14	3·97	6·60	3·81	13
6·92	6·02	4·99	12·27	4·72	7·38	4·65	16
8·26	6·06	6·07	13·68	5·44	8·34	5·48	19
9·54	6·39	7·12	15·61	6·15	9·35	6·36	23
10·88	7·09	8·13	18·17	6·40	9·66	7·13	26
12·10	8·37	9·16	21·35	—	—	7·84	29
13·08	9·66	10·05	24·58				

Back-titration of the Barium Hydroxide.—A colloidal platinum and the comparable coagulated (frozen) sol were titrated barium hydroxide in the usual manner. In each case the titra was stopped when the solutions contained the same amount of

base, *i.e.*, when they showed the same conductivities (C and D in Fig. 1A). Each solution was then immediately back-titrated with nitric acid. The results are set out in Table I and in the second part of Fig. 1. The divergence of the curves shows at once that a large amount of the removed base is brought back into solution by the acid. Now the fraction of barium hydroxide which can be so reclaimed at any given acid concentration can be calculated from the curves. Consider the points G and G′. Both solutions contained

FIG. 1.



B = Pt *sol*–NaOH *titration*. D = Pt *sol*–$Ba(OH)_2$ *titration*.
C = *Coagulated (frozen) sol*–$Ba(OH)_2$ (*or* NaOH) *titration*.

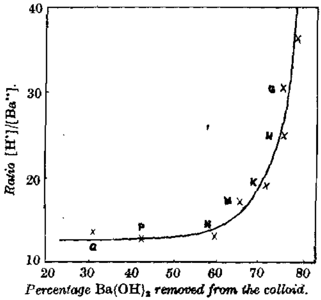
the same initial amount of free hexahydroxy-acid, and they both received the same excess of *free* barium hydroxide (since initially they corresponded to points C and D respectively), and as we are going to deal with the difference in conductivities at G and G′, the conductivities due to these substances, or rather to their salts, can be neglected. Of the $3{\cdot}4 \times 10^{-5}$ equiv. of extra acid added at G′, some remains as free acid and some has been replaced by barium nitrate. Let x represent the normality of the latter. Then $(0{\cdot}000034 - x)$ will represent the normality of the extra acid left as such. (The value of x may be greater than 0·000034, but it must be

less than 0·000099, which is the total acid concentration at G′.) The resulting conductivity due to these two factors is the difference in conductivity at G and G′, namely, zero. We therefore write that the conductivity of (0·000034 − x) equiv. of nitric acid plus that of x equivs. of barium nitrate equals zero. Using the relation: normality = x (in gemmhos)/ionic mobility × 1000 (Pennycuick, J., 1927, 2605), and using the mobility figures for 25°, $H^{\cdot}$ = 349·5, $\frac{1}{2}Ba^{\cdot\cdot}$ = 65·5, and NO'_3 = 71·3, we obtain

$$(0{\cdot}000034 - x) \times 421{,}000 + 137{,}000\, x = 0, \text{ whence } x = 0{\cdot}000050.$$

The normality of barium ion removed from the surface is therefore $5{\cdot}0 \times 10^{-5}$, and since the total amount taken up by the platinum

FIG. 2.



Percentage Ba(OH)₂ *removed from the colloid.*

had the value $6{\cdot}7 \times 10^{-5}N$, it follows that 25% of the barium i still held at the surface.

The full significance of these results is seen by calculating th above ratio over the whole range of the acid curves and plottin percentage of barium ion brought back into solution against th ratio [H˙]/[Ba˙˙]. Results for the points G, H, K, M, N, P, and are thus shown in Fig. 2. From these it is seen that some 60% the barium ion is brought back into solution at a low and practical constant hydrogen-ion concentration, approximately $1{\cdot}1 \times 10^{-5}$ of the remainder, another 15% is brought back fairly readily increasing the [H˙]/[Ba˙˙] ratio, but the final 25% of the surfa barium ion is replaceable (if at all) only as the acid concentrati becomes relatively high. Keeping in mind the figures alrea quoted, it can be concluded that from 20 to 25% of the base h ... salt of the hexahydroxy-acid, and that t

remainder is held at the surface in some less effective manner. In other words, a maximum of 20—25% of the surface of colloidal platinum particles consists of hexahydroxyplatinic acid.

The Nature of the Rest of the Surface.—It might be suggested that the rest of the surface is pure platinum and that the base is adsorbed thereby. This, however, does not appear to be correct, as is shown by the following experiment. Some platinum gauze and foil of a total surface area of 550 sq. cm. were thoroughly cleansed and placed at the bottom of an enlarged conductivity cell. This received 100 c.c. of conductivity water and then a steady addition of barium hydroxide. The specific conductivity was plotted against the barium hydroxide concentration, and the curve compared with that obtained in similar circumstances but without the platinum. A very slight deviation in the curves was obtained which corresponded to the removal by the pure platinum surface of approximately $0{\cdot}2 \times 10^{-5}$ equiv. of barium hydroxide. The platinum sols used in this work contained 0·130 g. of platinum per litre, and, taking the average radius of the colloid particle as 30×10^{-7} cm., one can calculate from the figures already quoted, that 550 sq. cm. of colloidal platinum surface in 100 c.c. of solution would remove $4{\cdot}6 \times 10^{-5}$ equiv. of barium hydroxide. Allowing for the inaccuracies involved in the calculation of the colloid surface, one must conclude that the removal of the extra base by the colloid cannot be ascribed to an adsorption at a pure platinum surface.

Now it is well known that platinum forms a whole series of oxides and oxy-acids (see Wöhler, *Z. anorg. Chem.*, 1904, **40**, 423; Bellucci, *ibid.*, 1905, **44**, 168), and there can be no doubt that during the preparation of colloidal platinum by the Bredig method a variety of oxidation products will be formed. The author has shown that, of these, some having strong acid properties [*e.g.*, $H_2Pt(OH)_6$] are bound at the surface and function as the colloid ionogenic stabilising agent. It is now suggested that the rest of the surface is composed of lower and less active oxides, which are too weak to form acids with water, but are able to form salts with bases. In connexion with this explanation, it should be noticed that Fuchs and Pauli (*Koll.-Chem. Beih.*, 1925, **21**, 412), working on colloidal gold, and Pauli and Valkó (*Kolloid-Z.*, 1926, **38**, 289), on colloidal silicic acid, conclude that the surfaces of these colloids contain inactive (non-ionogenic) molecules, which can be activated or rendered ionogenic by, *e.g.*, the addition of potassium bicarbonate. In fact, the latter workers have suggested that this property will be found to be common to all negative colloids.

On the assumption that part of the surface of colloidal platinum is covered by a weakly acidic oxide, and part by a strong acid,

the results obtained from the "back-titration" experiments follow naturally. *In the rest of this paper it will be shown that such a constitution explains the many important reactions of colloidal platinum in basic solution.*

The Action of Bases at the Colloid Surface.—The difference between the effects of sodium and barium hydroxides (Fig. 1A) may first be examined. On the gradual addition of sodium hydroxide, the free acid and the surface acid are first neutralised, and then the sodium hydroxide tends to combine with the surface oxide to form the corresponding salt. With colloidal gold and colloidal silicic acid (see references above) it has been shown that comparable reactions take place, which are indicated by the increase in the charge on the colloid particle. On the addition of further sodium hydroxide, a state will be reached in which the high charge on the colloid will suppress the reaction that tends to increase its charge, and some of the surface oxide will remain inactivated or uncombined. When the conditions are altered so as to decrease the charge on the particle, *e.g.*, by the addition of a sodium salt, more of the surface oxide will become activated. This can proceed until the whole of the oxide has reacted, and normal coagulation will then ensue. Experimental results will be quoted which amply support this view.

With barium hydroxide, the same reaction proceeds, but it is fundamentally affected by the strong electric force between the colloid ion and the bivalent barium ion (see Part V, preceding paper). In fact the activity of the colloid ion containing the barium salt is so small (as revealed by the low coagulation concentration of the barium ion) that the surface charge is never high, and the whole of the surface combination can take place at low barium hydroxide concentration. This explains the flat minimum in the titration curve (Fig. 1A), and moreover, it is in agreement with the observations on colloidal gold (Fuchs and Pauli, *loc. cit.*), where it is found that on the addition of barium hydroxide there is practically no initial increase in the charge on the gold particle.

The author is convinced that no good purpose will be served by interpreting the above results in terms of a difference in adsorption at the oxide surface. Although it is not improbable that here we have a connecting link between a physico-chemical surface reaction and an adsorption, explanations in terms of the latter, as applied to colloid surface reactions, have been so abused that the author feels that in such cases this term must be used with extreme caution.

(2) *The Coagulation by Electrolytes in Basic Solution.*

Univalent Bases and their Protective Action.—The protective action of univalent bases on negative colloids is quite general, and in the

preparation of colloidal gold and silver a weak solution of a univalent base is essential. This effect was for many years generally ascribed to an adsorption of the hydroxyl ion, but Pauli ("Eiweisskörper und Kolloide," J. Springer, Wien, 1926) has conclusively shown that it is due to the production of alkali complex salts which form the surface ionogens of the colloid.

If a solution of colloidal platinum is made alkaline with a univalent base, the alkali exerts a well-defined protective action on the colloid, and the coagulation concentration of different salts is increased remarkably. For example, when a platinum sol is made $0{\cdot}0067N$ with respect to sodium hydroxide, the coagulation concentration of salts with univalent kations is increased about 800%—in the case of sodium chloride from 0·004 to $0{\cdot}032N$. With a similar alkalinity ferric chloride shows a 90-fold increase in coagulation concentration, *viz.*, from 0·0001 to $0{\cdot}0090N$. As pointed out in the preceding paper, it is again evident that coagulation concentrations have no definite significance unless the p_H of the sol is defined.

In terms of the foregoing, the author interprets this general phenomenon as follows. In the absence of the base, the salt coagulation (see Part V) is due to the repression of the ionisation at the colloid surface of the salt of the strong platinic acid. The latter covers approximately one-fifth of the surface, and it would appear that the remaining four-fifths containing the oxide coating are unaffected during such coagulations. (Qualitative evidence in this direction is afforded by adding barium hydroxide to a barium chloride coagulum, whereupon it is found that a large amount of the base is completely removed by the precipitate.) If a univalent base be now added to the uncoagulated sol, part of the oxide is converted into the active surface ionogenic salt. Any attempt to repress the colloid charge by the addition of further foreign salt is accompanied by a further activation of the surface oxide and the restoration of the charge. This can proceed until the whole of the surface oxide has reacted, and further salt addition will then cause coagulation in the normal manner.

It is now evident why sodium hydroxide itself coagulates at a much higher concentration than sodium chloride, the respective concentrations being 0·052 and $0{\cdot}004N$.

As already explained, bivalent bases, owing to the electrostatic forces concerned, combine with the whole of the surface oxide at very low basic concentrations. The residual charging effect is therefore extremely small, and could only be detected in very favourable circumstances. It seems to be demonstrable in the case of acid clay suspensions (Oakley, J., 1927, 2054), but with colloidal platinum

sols the author was unable to show the protective action of barium hydroxide in any single case. It further becomes evident that the protective action of univalent bases on bivalent salts such as barium chloride and calcium nitrate must also be a minimum, for the bivalent hydroxide is immediately formed in the solution and reacts accordingly.

With salts of tervalent kations, the protective action of univalent bases is very pronounced. This is in keeping with results already recorded in Part V, where it was shown that the weak tervalent hydroxides play no important part (at the low concentrations concerned) in the coagulation process.

Hydrolysed Salts.—The general effect of hydrolysis on the coagulating power of a salt can now be explained. Where salts of univalent kations are hydrolysed to form basic solutions, the free base will have a protective action, and the coagulation concentration of such salts will be greater than that for unhydrolysed salts. For example, with a neutral sodium salt, the coagulation concentration of the sodium ion may be written as $0{\cdot}004N$; with sodium acetate, however, it is $0{\cdot}012N$, and with sodium cyanide $0{\cdot}018N$.

If a salt is hydrolysed to form an acid solution, the coagulating power may be greater or less than usual, according to whether the coagulating power of the hydrogen ion is greater or less than that of the kation of the salt. With ammonium chloride, for example, the hydrogen ion resulting from hydrolysis has a higher coagulating power than a univalent kation (approximately in the ratio 0·004 : 0·0002); accordingly ammonium chloride should be a better coagulant than neutral univalent salts. Actually, it has about twice the coagulating power of the neutral sodium salts. (With ammonium salts a second reaction may play some part, and this is receiving attention.) The coagulating power of tervalent kations, on the other hand, is much greater than that of the hydrogen ion, approximately in the ratio 0·0002 : 0·000024. Accordingly, with the highly hydrolysed ferric chloride, the production of free hydrochloric acid and the removal of ferric ion as insoluble or colloidal ferric hydroxide will result in this salt having a lower coagulating power than less hydrolysed tervalent salts. Ferric chloride is about a quarter as effective as the less hydrolysed aluminium sulphate in coagulating a platinum sol.

(3) *The Repeptisation of the Platinum Coagulum.*

It is well known that, in general, the coagulum produced [by] electrolytes is flocculent and by no means compact. This is the case with colloidal platinum; no matter what coagulating salt is used. With many colloids, the coagulum is of such a loose and o[pen]

structure that it can be repeptised with a suitable solution, or merely by washing. It has invariably been the case to speak of colloidal platinum as an irreversible colloid which, once coagulated, can never be repeptised (see Freundlich, "Colloid and Capillary Chemistry," English edn., 1926, p. 470). The author has been unable to find any case in the literature of the repeptisation of a platinum coagulum.

Now when a platinum sol in its natural (slightly acid) state is coagulated by a salt, it has been shown that the surface oxide is apparently unaffected by the process. Further, the fact that a barium chloride coagulum can still take up a large quantity of barium hydroxide indicates that the flocculent coagulum is sufficiently porous to allow the base to reach and react with the surface oxide. It therefore appeared that, if the foregoing explanation was valid, almost any platinum coagulum should be repeptisable by a univalent base. Experiment showed that this was the case.

Sols coagulated by salts with univalent kations, such as rubidium nitrate, sodium sulphate, and potassium chloride, were all readily repeptised by a small amount of sodium or potassium hydroxide. For example, a sol was completely coagulated by $0{\cdot}007N$-sodium chloride, and then completely repeptised when made $0{\cdot}0001N$ with respect to sodium hydroxide; moreover, the following experiment was performed. A sol was just coagulated with potassium chloride, the coagulum settling in one hour; it was then repeptised with a little sodium hydroxide, recoagulated with further potassium chloride, repeptised again, and so on. The action could be carried on until conditions demanded that the whole of the surface compound be formed, whereupon sodium hydroxide could exert no further repeptising action. In each case the repeptised solution was stable over a period of several months, and, further, the particles were still negatively charged.

As expected, the coagulum formed by a salt with a bivalent kation could not be thus repeptised. The reason for this is evident from a previous discussion.

The coagulum formed by a salt with a tervalent kation is readily repeptised. The explanation for this has also received attention. One important feature is that the repeptised sol (like every other such sol examined) still carries a negative charge. In excess of aluminium salt, it is well known that the colloid suffers a reversal of charge. With the low aluminium salt concentrations used, no unusual or abnormal features were revealed, and it is evident that at low concentrations these salts accord with the general theory.

It is significant that the whole of the above results on repeptisation were suggested by, and therefore are in accord with, the theory as outlined.

British bituminous coals that we have examined by similar methods have contained between 10 and 25% of spore exines and cuticles.

The exines of present-day spores, such as those of lycopodium, and the cuticles of present-day plants appear to be similar, both physically and chemically, to the corresponding plant structures in bituminous coals, the resistance of these parts of plants to the processes of decay, which enabled them to remain as entities in the coal-forming mass, having apparently been nearly proof against the processes of coalification. The results of an examination of modern plant cuticle have been published (Legg and Wheeler, J., 1925, **127**, 1412). A similar examination of modern spore exines and parallel studies of both exines and cuticles from coal, in accordance with the scheme outlined by Stopes and Wheeler ("The Constitution of Coal," H.M. Stationery Office, London, 1918), are in progress. An important property in relation to the present research is their decomposition at comparatively low temperatures, yielding a high proportion of their weight of oils.

In our previous papers (J., 1928, 2669, 3197), examples have been given of the behaviour of (1) hydrocarbons, (2) resins, and (3) ulmin compounds when a bituminous coal is destructively distilled in a vacuum, the yields of oils in particular being noted. Most of the coals we have examined have yielded a greater quantity of oils than can be accounted for by the distillation and decomposition of these constituents of the coal conglomerate, the excess of oils being generally unsaturated hydrocarbons. There remain the plant entities to be considered as oil-yielding constituents, the particular information required being the temperature range over which they decompose.

This information has been obtained by carrying out paralle distillations in a vacuum on samples of coal, from the same seam devoid of plant entities and containing known proportions o them, *i.e.*, on samples of vitrains and durains from the same seams The distillation of about 20 g. of spore exines separated from bituminous coal has given supplementary information.

In summarising the results of the present work, it is necessary t recapitulate some of the information previously recorded (*loc. cit* regarding the behaviour of the hydrocarbons, resins, and ulmi compounds in the coal conglomerate during destructive distillatio

With most bituminous coals containing more than 80% of carbo there is no extensive decomposition of any constituent below 300 Occluded gases are driven off up to 150°, and slight changes in th external groupings of the ulmin compounds may occur at lo temperatures, particularly if the coal has been "weathered resulting in the evolution of water and oxides of carbon. Betwe

220° and 300°, the major part of the free hydrocarbons in the coal (γ_1-compounds, extractable by solvents) distils unchanged.

The present work shows that at 300°, or just above, any plant entities the coal may contain begin slowly to decompose. With clarains, this decomposition may be difficult to detect, but it is easily recognisable with durains. The gaseous products are rich in oxides of carbon, and the liquids consist of water with much heavy oil, containing mainly unsaturated hydrocarbons and neutral oxygenated compounds. The temperature range over which this decomposition occurs, *viz.*, 310—350° (or 300—320° if the duration of heating is prolonged much beyond the normal), is nearly the same with all bituminous coals.

Above 300°, marked decomposition of the ulmin compounds begins, the products being gaseous paraffins, water, phenolic oils, and liquid aromatic and hydroaromatic compounds. This "active-decomposition point," which is well defined, increases with the "rank" of the ulmin compounds, and marks the breakdown of their nuclear structures. Over the range of bituminous coals studied (of carbon content 77—90%) it increased from 290° to 365°. The production of oils from the ulmin compounds is confined mainly to a temperature range of 25—30° above the active-decomposition point.

Above the active-decomposition point of the coal, ulmin compounds, organised plant entities, and resins decompose and distil simultaneously, yielding a complicated mixture of liquid products. It is difficult to trace the exact contribution made by each ingredient of the coal to this distillate, but the simultaneous liquation and decomposition (yielding hydrocarbon oils) of resins can be detected at about 325°, continuing to about 375°. This temperature range, which is the same for all the bituminous coals examined, may be lowered slightly and narrowed if the duration of heating is much prolonged. The amount of resins distilled unchanged is usually less than that extractable from the coal by solvents (γ_2-compounds), but it may approach that quantity if the coal also contains a fairly high proportion of plant entities yielding much hydrocarbon oils on decomposition, the presumption being that some of the resins are then "vapour-distilled."

The amounts and descriptions of the primary gaseous and liquid products of resolution of bituminous coals by heat are shown in Table I.

As the distillation is carried beyond 400°, increasingly large quantities of gases are evolved, the proportion of hydrogen they contain rapidly increasing. Nitrogen- and sulphur-containing compounds appear in small quantity in both gaseous and liquid products at all temperatures of distillation.

TABLE I.

The Resolution of Bituminous Coals by Heat.

Constituent.	Principal gaseous *products.*	Principal liquid products. *Character.*	*Quantity.*	Temperature *range.*
Free hydrocarbons.	Paraffins in small quantity.	Saturated and unsaturated hydrocarbons in nearly equal amount.	Equal to the original amount of free hydrocarbons in the coal.	225—300°
Resins	Paraffins and higher olefins.	Resins and unsaturated hydrocarbons.	Usually rather less than the original amount of resins in the coal.	325—375°
Structured plant entities (*e.g.*, spore exines).	Oxides of carbon and some paraffins.	Unsaturated hydrocarbons, neutral oxygenated compounds, and water.	About 30% of the original amount of plant entities in the coal.	300—320
Ulmin compounds.	Paraffins and some oxides of carbon.	Phenolic and acidic oils, unsaturated hydrocarbons, aromatic and hydroaromatic compounds, and water.	Decreases with increase in "rank" of the ulmins; 6—1% water and 3—0·05% phenols and acids with coals ranging from 77—90% carbon.	Decomposition point increases with "rank" of the ulmins: from 290—365° with coals ranging from 77—90% carbon. All oils distilled below 400°.

EXPERIMENTAL.

(1) *Comparative Distillations of Vitrains and Durains.*—The apparatus used for the distillation of 250-g. charges of the coals in a vacuum was that described in J., 1928, 2669. Large blocks of coal from several seams were obtained, and the vitrain and durain carefully separated from them by hand. For each coal, parallel distillations of these distinct components of banded bituminous coals were then carried out simultaneously. Two examples are recorded: (*a*) the Thick Seam (Brazils), from Hamstead Colliery; and (*b*) the Barnsley Seam, from Brodsworth Colliery. Analyses of these coals are given in Table II.

(*a*) *The Thick Seam.* With both the vitrain and the durain the stages of heating adopted were: 15—100°, 100—200°, 200—275°, and 25° intervals thereafter up to 400°. The coals were maintained at the higher temperature of each stage during 120 hours. The gases and liquids distilled at each stage were collected separately and analysed in the manner described in J., 1928, 2669. The neutral hydrocarbon oils, soluble in light petroleum, were treated with concentrated sulphuric acid and subsequently with fuming sulphuric acid to determine roughly the proportions of unsaturated, aromatic, and saturated hydrocarbons they contained. The results are recorded in Tables III and IV.

Little gas (mainly oxides of carbon) was yielded by either the vitrain or the durain below 290°. With the vitrain, a well-marked decomposition point was observed between 295° and 300°, a sudden

TABLE II.

Analyses of the Coals Used.

Coal.	Proximate analysis, %. Moist-ure.	Ash.	Volatile matter (ash-free, dry coal).	Ultimate analysis, % on "pure coal." C.	H.	N.	S.*	O.
Thick Seam, vitrain	13·4	1·3	37·5	78·3	5·15	1·02	1·01	14·52
Thick Seam, durain	6·4	6·0	35·1	80·9	4·71	1·08	0·97	12·34
Barnsley Seam, vitrain	6·4	1·3	33·0	81·2	5·31	1·34	1·03	11·12
Barnsley Seam, durain	3·5	4·0	36·1	82·7	5·23	1·42	1·06	9·59

Rational analysis, %.

Coal.	Hydro-carbons.	Resins.	Organised plant entities.	Ulmins.	Reactivity index for ulmins.
Thick Seam, vitrain	0·2	3·0	Nil	96·8	74
Thick Seam, durain	0·3	3·2	7·8	88·7	72
Barnsley Seam, vitrain ...	0·8	2·6	Nil	96·6	65
Barnsley Seam, durain ...	0·5	2·2	20·7	76·6	62

* Organic sulphur.

evolution of gaseous paraffins then occurring. With the durain, the evolution of gases increased between 290° and 310°, but the decomposition point was not well defined. A greater volume of gas was obtained from the durain than from the vitrain over this range, owing to the extensive evolution of carbon dioxide from the former. The durain yielded more carbon dioxide than the vitrain throughout the distillation, but much less paraffins below 350°.

Water of decomposition was evolved more freely by the durain than by the vitrain below 300°, but the reverse occurred above 310°.

Hydrocarbon oils were distilled from both coals below the active-decomposition point in quantities corresponding with their contents of free hydrocarbon (γ_1-compounds). The evolution of oils was accelerated just below 300°, above which the durain yielded more than the vitrain by reason of an extensive production of hydrocarbon oils between 300—350°. The vitrain yielded more phenolic oils. Analysis of the hydrocarbon oils from the two coals showed that in those from the vitrain aromatic hydrocarbons predominated, whilst those from the durain contained a high proportion of unsaturated hydrocarbons.

(*b*) *The Barnsley Seam.* The stages of heating adopted were 15—100°, 100—200°, 200—280°, 280—300°, thence 10° intervals up to 350°, and finally 350—375° and 375—400°. The coals were maintained at the higher temperature of each stage during 120 hours

Table III.

Gaseous Products of Distillation of Vitrain and Durain from Thick Seam.

(Volumes in c.c. per 100 g. of ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—300°.		300—325°.		325—350°.		350—375°.		375—400°.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
CO_2 (and H_2S)	6	20	19	35	90	317	118	396	89	759	90	1334	41	1375
Olefins	—	—	—	—	24	20	73	46	93	84	103	77	22	19
CO	1	3	4	10	42	52	62	44	88	57	134	69	135	45
H_2	—	—	—	—	—	—	—	—	96	48	77	91	117	140
Paraffins	—	1	1	4	110	65	329	74	628	408	1117	936	1332	1100

Table IV.

Liquid Products of Distillation of Vitrain and Durain from Thick Seam.

(% on ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—275°.		275—300°.		300—325°.		325—350°.		350—375°.		375—400°.		Total.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
Water	2·28	1·60	0·14	0·23	0·54	0·59	0·59	0·59	1·36	0·77	1·36	0·87	1·15	1·32	0·84	1·03	8·20	6·98
Light oils	—	—	0·05	0·04	0·18	0·16	0·19	0·16	0·33	0·32	0·33	0·32	0·23	0·32	0·19	0·16	1·50	1·48
Heavy oils	—	—	—	—	0·23	0·20	0·65	1·00	2·43	2·28	1·41	2·49	0·92	1·15	0·18	0·53	5·82	7·74
Fractionation of heavy oils.					V. (200—300°)			D. (200—300°)										
Sat. hydrocarbons	—	—	—	—	0·18			0·30	0·19	0·20	0·09	0·28	0·04	0·09	Trace	0·02	0·50	0·87
Unsat. hydrocarbons	—	—	—	—	0·15			0·34	0·43	0·84	0·07	0·76	0·13	0·08	0·02	0·05	0·80	2·07
Aromatic hydrocarbons	—	—	—	—	0·19			0·29	0·33	0·41	0·25	0·42	0·13	0·30	0·06	0·02	0·95	1·62
Acidic oils	—	—	—	—	0·08			0·04	0·28	0·08	0·05	0·13	0·10	0·05	0·05 }	0·13 (acidic and phenolic oils together)	0·56	0·30
Phenolic oils	—	—	—	—	0·14			0·14	0·71	0·24	0·53	0·29	0·20	0·26	— }		1·67	1·06
Bases	—	—	—	—	0·02			0·02	0·07	0·04	0·04	0·04	0·04	0·04	0·01	0·02	0·18	0·16
Ether-sol. oils	—	—	—	—	0·03			0·04	0·12	0·35	0·20	0·43	0·09	0·15	0·02 }	0·08 (ether-sol. and $CHCl_3$-sol. oils together)	0·46	1·05
$CHCl_3$-sol. oils	—	—	—	—	0·01			—	0·04	0·06	0·05	0·10	0·03	0·03	Trace }		0·13	0·19
Loss during fractionation	—	—	—	—	0·09			0·12	0·26	0·06	0·13	0·06	0·07	0·15	0·02	0·03	0·56	0·42

Table V.

Gaseous Products of Distillation of Vitrain and Durain from Barnsley Seam.

(Volumes in c.c. per 100 g. of ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	15—100°.		100—200°.		200—280°.		280—300°.		300—310°.		310—320°.		320—330°.		330—340°.		340—350°.		350—375°.		375—400°.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
CO_2 (and H_2S)	8	6	17	17	25	29	23	42	22	75	28	53	41	33	42	26	39	30	72	71	50	42
Olefins	—	—	—	—	3	3	9	11	20	31	25	45	49	42	41	35	34	33	58	46	20	16
CO	4	1	8	1	10	11	8	18	18	33	19	20	23	11	31	15	32	20	73	43	57	37
H_2	—	—	—	—	—	—	—	—	—	—	2	4	2	3	4	9	8	17	65	92	124	175
Paraffins	36	24	9	8	12	10	34	45	90	174	159	217	300	243	455	280	503	322	1230	895	1440	1060

Table VI.

Liquid Products of Distillation of Vitrain and Durain from Barnsley Seam.

(% on ash-free, dry coal. V = vitrain; D = durain.)

Temp. range.	100—200°.		200—280°.		280—300°.		300—310°.		310—320°.		320—330°.		330—340°.		340—350°.		350—375°.		375—400°.		Total.	
	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.	V.	D.
Water	0·13	0·21	0·23	0·85	0·14	0·29	0·22	0·60	0·35	0·54	0·39	0·22	0·56	0·27	0·48	0·21	0·84	0·60	0·78	0·79	4·07	4·08
Light oils	0·05	0·15	0·29	0·08	0·17	0·11	0·13	0·32	0·14	0·40	0·24	0·22	0·22	0·17	0·18	0·22	0·30	0·27	0·17	0·20	1·89	2·14
Heavy oils	—	—	0·15	0·23	0·25	0·65	0·48	3·36	0·58	4·43	0·73	1·47	0·65	0·90	0·37	0·62	0·32	0·72	0·10	0·14	3·60	12·52
Fractionation of heavy oils.			V. (200—300°)			D. (200—300°)																
Sat. hydrocarbons	—	—	0·10			0·12	0·07	0·19	0·06	0·22	0·03	0·11	0·02	0·06	Trace	0·04	Trace	0·02	—	Trace	0·28	0·75
Unsat. hydrocarbons ...	—	—	0·14			0·80	Trace	1·24	0·03	1·67	0·06	0·34	0·07	0·24	0·06	0·17	0·06	0·14	—	0·06	0·44	4·15
Aromatic hydrocarbons	—	—	0·08			0·12	0·10	0·28	0·11	0·35	0·09	0·16	0·03	0·12	0·02	0·10	0·03	0·06	0·02	Trace	0·45	1·19
Acidic oils	—	—	—			0·01	0·02	0·05	0·04	0·04	0·06	0·04	0·06	0·01	0·02	— }	0·10 (acidic + phenolic)	—	—	—	0·20	0·15
Phenolic oils	—	—	—			0·04	0·08	0·19	0·12	0·10	0·16	0·10	0·14	0·06	0·11	0·03 }		0·09	—	—	0·71	0·70
Bases	—	—	—			0·01	0·01	0·04	0·01	0·04	0·02	0·03	0·01	0·01	0·01	—	—	0·06	—	—	0·06	0·10
Oxygenated compounds	—	—	0·04			0·13	0·05	0·43	0·04	0·50	0·05	0·22	0·03	0·10	0·02	0·08	0·02	0·14	—	0·04	0·25	1·64
Ether-sol. oils	—	—	—			0·07	0·06	0·40	0·06	0·63	0·14	0·19	0·20	0·15	0·08	0·06	0·05 }	0·10 (ether-sol. + $CHCl_3$-sol.)	0·08 (ether-sol. + $CHCl_3$-sol.)	0·02 (ether-sol. + $CHCl_3$-sol.)	{0·67	1·56
$CHCl_3$-sol. oils	—	—	—			0·03	0·03	0·19	0·02	0·30	0·06	0·07	0·04	0·07	0·02	0·02	0·01 }				{0·18	0·74
Loss during fractionation	—	—	0·04			0·05	0·03	0·85	0·09	0·49	0·06	0·22	0·05	0·08	0·03	0·12	0·05	0·11	—	0·03	0·35	1·55

except at 300—310° and 310—320°, for which the duration was 240 hours, the shorter time being insufficient to distil all the oils from the durain at those temperatures. The gases and liquids evolved at each stage were collected separately. In the examination of the neutral hydrocarbon oils, oxygenated compounds were removed by treatment with ferric chloride, according to Robinson's method (J., 1925, **127**, 768). The results are recorded in Tables V and VI. They were similar to those obtained with the Thick Seam, but there was a greater contrast between the behaviour of the vitrain and the durain because the latter contained a higher proportion of plant entities than did the durain of the Thick Seam.

The active-decomposition point, well marked with the vitrain but less distinct with the durain, was at 305—310°. Above this temperature the evolution of gases rapidly increased, paraffins predominating. Between 300—320° the durain yielded considerably more gases than the vitrain, the excess being due to carbon dioxide. The durain also yielded much more water of decomposition than the vitrain over this range. Above 320°, the evolution of gases, particularly of the paraffins, increased more rapidly with the vitrain than with the durain, and the former yielded the greater quantity of water.

The yields of oils from the two coals were markedly different, the durain producing the greater quantity, particularly over the range 300—320° (*i.e.*, the range over which it evolved the greater quantities of gases and water). The oils from the vitrain, apart from phenolic compounds, consisted mainly of aromatic hydrocarbons. The oils from the durain contained less phenolic compounds and the hydrocarbons were mainly unsaturated.

(2) *Distillation of Spore Exines from Bituminous Coal.*—We are indebted to Dr. V. H. Legg for a supply of megaspore exines separated by him from the durain of the Top Hard Seam, East Kirkby. The mode of separation involved the gradual oxidation by hydrogen peroxide, and subsequent dissolution in potassium hydroxide solution, of the matrix of ulmin compounds in which the megaspores were embedded. Partial oxidation of the megaspores must be presumed, though their appearance was unchanged by this treatment. The retort when filled contained 17 g. of spore exines. The distillation was carried out by stages as recorded in Table VII, the duration of heating at the higher temperature of each stage being 120 hours.

Heavy oils began to distil at 280° and appeared in greatest quantity over the range 300—360°. Water and large volumes of gas, containing a high proportion of paraffins and carbon dioxide, accompanied the oils, which consisted mainly of unsaturated and aromatic hydrocarbons and oxygenated compounds. The hydrocarbon oi

TABLE VII.

Gaseous and Liquid Products of Distillation of Megaspore Exines.

(Gases : c.c. per 100 g. Liquids : % by weight.)

Temp. range.	100—200°.	200—300°.	300—330°.	330—360°.	360—400°.	Total.
CO_2 (*and* H_2S)	1170	1269	177	209	179	3004
Olefins	7	34	66	273	299	679
CO	112	277	155	190	188	922
H_2	—	—	42	185	624	851
Paraffins	12	122	522	1440	1390	3476
Water	2·9	3·5	5·3	1·5	0·7	13·9
Light oils	0·3	0·3	1·4	1·2	1·0	4·2
Heavy oils	Nil	1·5	6·7	5·5	3·0	16·7
Fractionation of heavy oils.						
Sat. hydrocarbons	—	Trace	0·5	0·4	0·2	1·1
Unsat. hydrocarbons	—	0·8	2·7	1·7	0·9	6·1
Aromatic hydrocarbons	—	0·2	0·9	0·7	0·4	2·2
Phenolic and acidic oils	—	Trace	0·3	0·3	0·1	0·7
Bases	—	,,	0·2	0·2	0·1	0·5
Oxygenated compounds	—	0·2	1·2	0·7	0·4	2·5
Ether- and chloroform-soluble oils	—	Trace	0·3	1·1	0·5	1·9
Loss during fractionation	—	0·3	0·6	0·4	0·4	1·7

like those from the two durains, darkened on exposure to the air, oxygenated compounds being readily formed from them.

The products of distillation of megaspore exines thus provide, over the significant temperature range, the difference in character between the gaseous and liquid products of distillation of durain and vitrain from the same coal.

The work described in this paper forms part of a research on the constitution of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, January 30th, 1929.*]

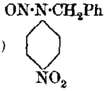
XCII.—*The Nitration of Phenylbenzylamine Derivatives.*

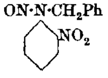
By JOSEPH REILLY, PETER J. DRUMM, and TIMOTHY V. CREEDON.

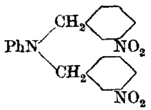
IN a recent paper (J., 1928, 563) the authors showed that, on nitration of benzylaniline and dibenzylaniline under similar conditions, the former yielded only the nitrate of the base. Nitration

of the secondary amine in sulphuric acid solution led to the formation of phenyl-3-nitrobenzylamine together with a smaller amount of the corresponding 4-nitro-derivative.

That work is now extended to include the nitration of phenylbenzylamine derivatives in which the imino-hydrogen is replaced by acidic and other groups. Unlike the parent substance, nitrosobenzylaniline is nitrated directly or in acetic acid solution with remarkable ease, giving nitroso-4-nitrophenylbenzylamine (I) as the main product and a small amount of the nitroso-2-nitro-compound (II).

(I.) 


(II.)

 (III.)

There are conflicting views in the literature with regard to the orientation of the nitration products of benzylalkylanilines. Schultz, Rohde, and Bosch (*Annalen*, 1904, **334**, 242) state that benzylethylaniline in sulphuric acid solution is nitrated in the benzyl ring, whereas Gnehm and Scheutz (*J. pr. Chem.*, 1901, **63**, 426), who worked under identical conditions, assign the nitro-group to the aniline ring. The nitration of benzyl-*n*-butylaniline is in line with the results of the former workers, the main product isolated being phenyl-3-nitrobenzyl-*n*-butylamine.

Nitration of dibenzylaniline in acetic acid solution gives mainly 2 : 4-dinitrophenyldibenzylamine and a very small amount of the 2 : 6-dinitro-compound (Desai, *J. Indian Chem. Soc.*, 1928, **5**, 425). Evidence of the formation of either of these nitro-derivatives in the hitherto unrecorded nitration of dibenzylaniline in sulphuric acid solution has not been obtained, but instead the authors have isolated a new dinitro-derivative, which has been shown by direct synthesis to be *phenyldi*-m-*nitrodibenzylamine* (III).

The experimental evidence supports the view that nitration of phenylbenzylamine derivatives directly (*i.e.*, as bases) leads to the formation of nitro-derivatives substituted in the aniline ring, whereas nitration through the salt promotes substitution in the benzyl nucleus.

EXPERIMENTAL.

Nitration of Nitrosobenzylaniline.—Nitrosobenzylaniline (5 g.) was slowly added, with stirring, to nitric acid (*d* 1·42; 25 c.c.) at 0—5°. When the mixture was poured on ice, a reddish, partly solid product was obtained from a solution of which in hot alcohol there separated,

on cooling, yellow needles (3·4 g.), m. p. 108—109°, of nitroso-4-nitrophenylbenzylamine (Found : N, 16·1. Calc. for $C_{13}H_{11}O_3N_3$: N, 16·3%). This constitution follows from the fact that, on heating with an alcoholic solution of either hydrochloric acid or potassium hydroxide, the nitroso-group was eliminated and a substance obtained, m. p. 143—144°, a mixture of which with the 4-nitrophenylbenzylamine of Meldola and Streatfeild (*Ber.*, 1886, **19**, 3250) showed no depression in melting point.

The alcoholic mother-liquor, on dilution with water, gave an oil which did not crystallise. This was boiled with alcoholic hydrochloric acid : from the solution, on standing, orange-coloured plates (1 g.), m. p. 74·5°, separated, which showed no depression in melting point when mixed with 2-nitrophenylbenzylamine (m. p. 74·5°).

On adding nitric acid (*d* 1·42; 20 g.) to a solution of nitrosobenzylaniline (10 g.) in glacial acetic acid (60 c.c.), considerable heat was evolved, the temperature rising from 18° to 40°. From the reddish solution, nitroso-4-nitrophenylbenzylamine (7 g.) was obtained on cooling. From the mother-liquor, 2-nitrophenylbenzylamine (1·5 g.) was obtained in the manner already described.

Nitration of Phenylbenzyl-n-*butylamine in Mixed Acids.*—To a well-cooled solution of phenylbenzyl-*n*-butylamine (9 g.) in concentrated sulphuric acid (100 c.c.) was added, with stirring, a solution of nitric acid (*d* 1·51; 2·2 g.) in concentrated sulphuric acid (30 c.c.), the temperature being maintained at 0°. The mixture was stirred for 6 hours at 0° and poured on ice. The clear solution, when made alkaline in the cold with sodium carbonate solution, gave a dark oil, which was extracted with chloroform and dried with anhydrous potassium carbonate. The chloroform on evaporation left a viscous oil which, after inoculation with a crystal of *phenyl-3-nitrobenzyl*-n-*butylamine* and standing in the ice-chest for a week, set to a semi-solid mass. This, drained on a porons plate, left a solid (6 g.), which was ohtained from alcohol in bright yellow plates, m. p. 44—45° (Found : N, 9·8. $C_{17}H_{20}O_2N_2$ requires N, 9·9%).

The above nitro-compound was identical in all respects with phenyl-3-nitrobenzyl-*n*-butylamine synthesised by heating 3-nitrobenzyl chloride (1 mol.) and *n*-butylaniline (2 mols.) for 3 hours at 130—140°. The product was made alkaline by addition of sodium hydroxide solution and distilled in steam. The residual oil slowly solidified, and separated from alcohol in yellow plates, m. p. 44—45° (Found : N, 9·9%), readily soluble in chloroform, ether, and benzene and moderately easily soluble in cold ethyl alcohol.

Nitration of Dibenzylaniline in Mixed Acids.—In the nitration of dibenzylaniline the use of one molecular proportion of nitric acid left

much initial material unchanged and gave substantially the same product as when two molecular proportions were used. Potassium nitrate gave more satisfactory results than fuming nitric acid.

To a solution of dibenzylaniline [recrystallised from alcohol; m. p. 69—70° as against 67° recorded by Matzudaira (*Ber.*, 1887, **20**, 1611) and 71° by Wedekind (*Ber.*, 1899, **32**, 522)] (10 g.) in sulphuric acid (100 c.c.), potassium nitrate (7·4 g.) was slowly added at room temperature with stirring. There was no appreciable rise in temperature. After 12 hours, the mixture was poured on ice. The sulphate of the nitro-compound which separated was converted into the base by means of sodium hydroxide solution. The yellow residue (10 g.) obtained after trituration with ether was separated into two parts by repeated fractional crystallisation from ethyl alcohol–ethyl acetate. The less soluble portion (2·8 g.) consisted of canary-yellow prisms, m. p. 128—129° (Found: N, 11·5. $C_{20}H_{17}O_4N_3$ requires N, 11·6%), and was identified as *phenyldi*-m-*nitrodibenzylamine* (III) by the synthesis described below. The second fraction melted at 100—105°. No other definite substance was isolated. The melting point of the fraction m. p. 100—105° was not depressed by addition of phenyldi-*m*-nitrodibenzylamine. Repeated extraction of this fraction with ethyl alcohol–ethyl acetate removed small amounts of phenyldi-*m*-nitrodibenzylamine, but the other nitro-compounds present were not identified. It melted at 80—90° when mixed with 2 : 4-dinitrophenyldibenzylamine (m. p. 107°).

Synthesis of Phenyldi-m-*nitrodibenzylamine* (III).—Aniline (1 mol.) and *m*-nitrobenzyl chloride (2 mols.) were heated in alcoholic solution for 2 hours. The alcohol was removed, a concentrated aqueous solution of sodium carbonate added, and the mixture boiled for 8 hours. The product, which solidified on cooling, was extracted with warm alcohol; the yellow insoluble portion separated from alcohol–ethyl acetate in canary-yellow prisms, m. p., alone or mixed with the above nitro-compound, 129—130°. Phenyldi-*m*-nitrodibenzylamine is readily soluble in chloroform, benzene, and ethyl acetate and sparingly soluble in cold alcohol, acetic acid, and ether.

We wish to thank Mr. William Rintoul, F.I.C., of Imperial Chemical Industries, Ltd. (Nobel's Explosive Co.) for providing the dibenzylaniline, and the Chemical Society for a grant which has partly defrayed the cost of this work.

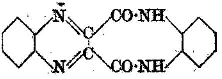
UNIVERSITY COLLEGE, CORK. [*Received, January 28th, 1929.*]

XCIII.—*The Action of* o-*Phenylenediamines upon Dihydroxytartaric Acid.*

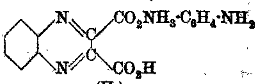
By Frederick Daniel Chattaway and William Gerald Humphrey.

In the course of his investigation of the quinoxalines, Hinsberg condensed *o*-phenylenediamine (*Ber.*, 1894, **27**, 2185) and 3 : 4-tolylenediamine (*Annalen*, 1887, **237**, 353) with sodium dihydroxytartrate and obtained, on acidification of the resulting solutions, quinoxaline-2 : 3-dicarboxylic acid and 6-methylquinoxaline-2 : 3-dicarboxylic acid respectively. Attempts to obtain the bases themselves from these acids by elimination of carbon dioxide were unsuccessful.

A reinvestigation of the course of this reaction has shown that it is not so simple as Hinsberg supposed. When sodium dihydroxytartrate is heated with an aqueous solution of *o*-phenylenediamine, two molecules of the diamine react with one molecule only of the salt, forming *quinoxaline-2 : 3-dicarboxy-*o*-phenylenediamide* (I); sodium dihydroxytartrate is only very sparingly soluble in water, and any excess above one molecular proportion remains in suspension unchanged. When the filtered alkaline solution is partly neutralised with hydrochloric acid, the diamide (I) separates as a colourless crystalline powder. It is stable in neutral solution, and dissolves readily in cold dilute aqueous alkali, from which it is reprecipitated on addition of a deficiency of acid. It dissolves in hot dilute hydrochloric acid (1 : 50), but on cooling, the *o-phenylenediamine* salt (II) of quinoxaline-2 : 3-dicarboxylic acid separates; whereas if it is dissolved in hot, moderately concentrated hydrochloric acid (1 : 1), quinoxaline-2 : 3-dicarboxylic acid separates on cooling, *o*-phenylenediamine hydrochloride remaining in solution. The salt (II) and the dicarboxylic acid may consequently be obtained directly from the original yellow condensation solution, the former by making the solution weakly acid with hydrochloric acid, and the latter by saturating it with gaseous hydrogen chloride.



(I.)

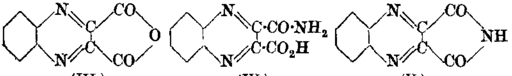


(II.)

Attempts to acetylate or benzoylate the amide (I) by the usual methods also cause decomposition, with formation of the diacetyl or the dibenzoyl derivative of *o*-phenylenediamine.

Quinoxaline-2 : 3-dicarboxylic acid, when heated with acetic anhydride, is converted into *quinoxaline-2 : 3-dicarboxylic anhydride*

(III), and the action of dry ammonia upon this anhydride in benzene suspension yields the *ammonium* salt of *quinoxaline*-2 : 3-*dicarboxyamic acid* (IV), from which the *acid* itself may be obtained on acidification. This amic acid is converted into the corresponding *imide* (V) on being heated above its melting point, and into the *acetyl* derivative of the imide on boiling with acetic anhydride.



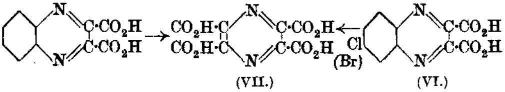
(III.) (IV.) (V.)

On being heated above its melting point, quinoxalinedicarboxylic acid decomposes, evolving carbon dioxide and yielding a small quantity (10%) of quinoxaline; better yields (30%) of this base are obtained by heating the ammonium salt of the acid. In common with other nitrogen bases, quinoxaline forms a stable, well-crystallised *mono-tetrachloroiodide*.

p-Chloro-*o*-phenylenediamine (2 mols.) reacts similarly with sodium dihydroxytartrate (1 mol.), forming first 6-*chloroquinoxaline*-2 : 3-*dicarboxy*-p-*chloro*-o-*phenylenediamide*, from which the p-*chloro*-o-*phenylenediamine* salt of 6-chloroquinoxaline-2 : 3-dicarboxylic acid, and 6-*chloroquinoxaline*-2 : 3-*dicarboxylic acid* (VI) are obtained by heating with dilute and with concentrated hydrochloric acid respectively. *p*-Bromo-*o*-phenylenediamine reacts similarly to give the corresponding *bromo*-compounds. These halogen-substituted derivatives are considerably less soluble than the unsubstituted compounds, and are therefore more readily prepared and purified otherwise their reactions are analogous. 6-Chloro- and 6-bromo quinoxaline-2 : 3-dicarboxylic acid melt with decomposition anc yield 6-*chloro*- and 6-*bromo-quinoxaline* respectively; as with th unsubstituted acid, better yields are obtained by heating th ammonium salts.

The oxidation of quinoxaline derivatives was attempted b Hinsberg (*Annalen*, 1887, **237**, 353) but without success; Gabriel an Sonn, however, succeeded in oxidising quinoxaline with alkalin permanganate to pyrazine-2 : 3-dicarboxylic acid (*Ber.*, 1907, **4** 4850); it has been found that quinoxaline-2 : 3-dicarboxylic aci and also 6-chloro- and 6-bromo-quinoxaline-2 : 3-dicarboxylic acid are similarly oxidised, yielding pyrazinetetracarboxylic acid (VII This acid was prepared by Wolff (*Ber.*, 1893, **26**, 721) by th oxidation of tetramethylpyrazine, but no details or analyses ar given; some difficulty was evidently experienced in preparing it, an Kalischer (*Ber.*, 1895, **28**, 1516) failed to isolate it in a pure conditio from the products of oxidation of dimethyldiethylpyrazine.

Pyrazinetetracarboxylic acid forms a sparingly soluble, well-crystallised *dipotassium dihydrogen* salt and a *tetraethyl* ester.



(VII.) (VI.)

Experimental.

Quinoxaline-2 : 3-dicarboxy-o-phenylenediamide (I).—A fine suspension of 7 g. of sodium dihydroxytartrate (1 mol. + excess) in a solution of 5·4 g. of *o*-phenylenediamine (2 mols.) in 50 c.c. of water was heated at 90° for ½ hour, and the hot yellow filtered solution was partly neutralised by the slow addition of 2·5 c.c. of concentrated hydrochloric acid (1 mol.) with vigorous stirring. The *diamide* (I), which separated on cooling, crystallised from boiling water (animal charcoal), in which it was very easily soluble, in glistening, colourless, rhombic plates, m. p. 184° (decomp.); yield, 3 g. (Found: C, 66·1; H, 3·2; N, 19·3. $C_{16}H_{16}O_2N_4$ requires C, 66·2; H, 3·4; N, 19·3%).

o-*Phenylenediamine Salt of Quinoxaline-2 : 3-dicarboxylic Acid* (II).—In an experiment similar to the above, the hot filtered solution was cooled and acidified with 10 c.c. of concentrated hydrochloric acid (4 mols.); the thick pulp of the o-*phenylenediamine* salt of quinoxaline-2 : 3-dicarboxylic acid obtained was recrystallised from boiling water (animal charcoal), in which it was very easily soluble, separating in lemon-yellow, compact prisms, m. p. 186° (decomp.); yield, 5 g. (Found: C, 59·2; H, 4·4; N, 17·0. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·3; N, 17·2%). This salt is also readily prepared by mixing aqueous or alcoholic solutions of quinoxalinedicarboxylic acid and *o*-phenylenediamine.

Quinoxaline-2 : 3-dicarboxylic Acid.—14 G. of sodium dihydroxytartrate (1 mol.) were dissolved in a hot solution of 11 g. of *o*-phenylenediamine (2 mols.) in 100 c.c. of water, and the filtered solution was saturated with hydrogen chloride. Quinoxaline-2 : 3-dicarboxylic acid, which separated as a crystalline powder, was recrystallised from boiling water (animal charcoal), in which it was moderately easily soluble, separating in long colourless prisms containing two molecules of water (yield, 8·5 g. or 70%). This water is lost at 110°; the anhydrous acid melts at 190° (decomp.). Half of the *o*-phenylenediamine is inevitably lost as the hydrochloride.

The *ethyl* ester prepared by boiling the acid with alcohol containing 2% of hydrogen chloride, separated from alcohol, in which it was very

easily soluble, in small, slender, colourless prisms, m. p. 83° (Found: N, 10·1. $C_{14}H_{14}O_4N_2$ requires N, 10·2%).

The *ammonium* salt separated as a white pulp when a few drops of aqueous ammonia (*d* 0·880) were added to an alcoholic solution of the acid. It is very easily soluble in water, but is rather sparingly soluble in glacial acetic acid, from which it crystallises in long, slender, colourless prisms (Found: C, 47·3; H, 4·5. $C_{10}H_{12}O_4N_4$ requires C, 47·6; H, 4·75%); these blacken and decompose at 220—230°, yielding quinoxaline.

Quinoxaline-2 : 3-dicarboxylic anhydride (III) separated in very pale yellow, long prisms when a solution of 2 g. of the acid in 20 c.c. of acetic anhydride was cooled (Found: N, 13·9. $C_{10}H_4O_3N_2$ requires N, 14·0%). It decomposes and chars at 250—260°.

Quinoxaline-2 : 3-dicarboxyamic Acid (IV).—Dry ammonia was passed for several hours through a fine suspension of 8 g. of the anhydride (II) in 150 c.c. of benzene. The anhydride gradually dissolved and the ammonium salt of the amic acid, which separated as a white crystalline powder, was filtered off and dissolved in cold water, and the *acid* (IV) precipitated by addition of dilute hydrochloric acid. It crystallised from alcohol, in which it was moderately easily soluble, in small, colourless, rhombic prisms, m. p. 190—195° (decomp.) (Found: C, 55·1; H, 3·1; N, 19·4. $C_{10}H_7O_3N_3$ requires C, 55·3; H, 3·2; N, 19·35%).

This acid crystallises from acetic acid, in which it is very easily soluble, in colourless, compact, hexagonal prisms containing one molecule of acetic acid; if heated slowly, the crystals evolve acetic acid at about 100°, and melt identically with the acid crystallised from alcohol; the crystals slowly effloresce and become opaque on exposure to air (Found: loss at 120°, 21·8. $C_{10}H_7O_3N_3,C_2H_4O_2$ requires loss, 21·65%).

Quinoxaline-2 : 3-dicarboxyimide (V) was prepared by heating the above acid at 185° (oil-bath) for 20 minutes and finally at 205°. The resulting brown mass crystallised from acetic acid (animal charcoal), in which it was rather sparingly soluble, in very pale yellow, rhombic prisms, decomp. about 260° (Found: C, 60·2; H, 2·3; N, 21·2. $C_{10}H_5O_2N_3$ requires C, 60·3; H, 2·5; N, 21·1%).

The *acetyl* derivative of the above imide, prepared by crystallising 3 g. of the acid (IV) from 100 c.c. of boiling acetic anhydride, separated in colourless, irregular leaflets, decomp. about 220° (Found: C, 59·7; H, 3·0; N, 17·4. $C_{12}H_7O_3N_3$ requires C, 59·75; H, 2·9; N, 17·4%).

Preparation of Quinoxaline from Quinoxaline-2 : 3-dicarboxylic Acid.—The ammonium salt (5 g.) of the acid was heated at 220—240° (oil-bath) for ½ hour, and the product distilled in steam. Addition of

concentrated aqueous caustic potash to the distillate gave quinoxaline in colourless, feathery needles, m. p. 27°, b. p. 225—226° (*yield*, 30%).

Quinoxaline Mono-tetrachloroiodide.—A solution of tetrachloroiodic acid (excess), prepared by passing chlorine through a fine suspension of 1·5 g. of iodine in 20 c.c. of concentrated hydrochloric acid, was added to 0·5 g. of quinoxaline in 2 c.c. of concentrated hydrochloric acid. The *tetrachloroiodide*, which separated immediately, crystallised from acetic acid (containing a little tetrachloroiodic acid), in which it was moderately easily soluble, in bright yellow, rhombic plates, m. p. 125—130° (decomp.) (Found: Cl, 35·7. $C_8H_6N_2,HICl_4$ requires Cl, 35·5%). It does not lose halogen on keeping and can be dried in a desiccator over calcium chloride.

6-*Chloroquinoxaline*-2 : 3-*dicarboxy*-p-*chloro*-o-*phenylenediamide* and 6-*bromoquinoxaline*-2 : 3-*dicarboxy*-p-*bromo*-o-*phenylenediamide* (formulæ as I), prepared in a similar manner to the corresponding unsubstituted compound, crystallise from water, in which they are rather sparingly soluble, in colourless irregular plates, m. p. 207° (decomp.) (Found: N, 15·7; Cl, 19·9. $C_{16}H_8O_2N_4Cl_2$ requires N, 15·6; Cl, 19·8%), and 198° (decomp.) (Found: N, 12·35; Br, 35·8. $C_{16}H_8O_2N_4Br_2$ requires N, 12·5; Br, 35·7%), respectively.

The p-*chloro*-o-*phenylenediamine* salt of 6-chloroquinoxaline-2 : 3-dicarboxylic acid and the p-*bromo*-o-*phenylenediamine* salt of 6-bromoquinoxaline-2 : 3-dicarboxylic acid (formulæ as II), prepared in a similar manner to the corresponding unsubstituted compound, crystallise from water, in which they are rather sparingly soluble, in lemon-yellow, elongated, rhombic plates, m. p. 205° (decomp.) (Found: N, 13·9; Cl, 18·0. $C_{16}H_{12}O_4N_4Cl_2$ requires N, 14·2; Cl, 18·0%), and 199° (decomp.) (Found: C, 39·9; H, 2·6; N, 11·3; Br, 33·1. $C_{16}H_{12}O_4N_4Br_2$ requires C, 39·7; H, 2·5; N, 11·6; Br, 33·1%), respectively.

6-*Chloroquinoxaline*-2 : 3-*dicarboxylic acid* (VI) was prepared in a similar manner to the corresponding unsubstituted compound. It crystallises from water, in which it is moderately easily soluble, in small, slender, colourless prisms containing two molecules of water, which are lost at 110° (Found: loss, 12·8. $C_{10}H_5O_4N_2Cl,2H_2O$ requires loss, 12·5%); the anhydrous acid melts at 175° (decomp.) (Found: C, 47·7; H, 2·0; N, 10·9; Cl, 13·9. $C_{10}H_5O_4N_2Cl$ requires C, 47·5; H, 2·0; N, 11·1; Cl, 14·05%).

The *anhydride* (formula as III), prepared by crystallising 2 g. of the acid from 20 c.c. of boiling acetic anhydride, separates in very faintly yellow, rhombic plates, decomp. 235—240° (Found: Cl, 15·15. $C_{10}H_3O_3N_2Cl$ requires Cl, 15·15%).

The *ethyl hydrogen* ester, prepared by dissolving 2 g. of the

anhydride in 5 c.c. of boiling alcohol, separates on addition of water in colourless, long, slender prisms, m. p. 159° (Found: Cl, 12·6. $C_{12}H_9O_4N_2Cl$ requires Cl, 12·65%). The *ethyl* ester, prepared by boiling 2 g. of the anhydride with 5 c.c. of alcohol, containing hydrogen chloride, for 8 hours, crystallises from 25% aqueous alcohol, in which it is moderately easily soluble, in small, colourless, rhombic plates, m. p. 60° (Found: Cl, 11·4. $C_{14}H_{13}O_4N_2Cl$ requires Cl, 11·5%).

The *ammonium* salt, which separates as a white pulp when aqueous ammonia (*d* 0·880) is added to an alcoholic solution of the acid, crystallises from acetic acid, in which it is rather sparingly soluble, in hair-like needles, decomp. 215—225° (Found: Cl, 12·3. $C_{10}H_{11}O_4N_4Cl$ requires Cl, 12·4%).

6-*Chloroquinoxaline*.—6-Chloroquinoxaline-2 : 3-dicarboxylic acid decomposes on being heated to 190°, giving a 20% yield of 6-chloroquinoxaline. An improved yield is obtained by heating the corresponding ammonium salt, the method being similar to that employed in the preparation of quinoxaline; the 6-*chloroquinoxaline* was isolated by steam distillation and separated from the distillate in fine colourless needles, m. p. 60° (Found: C, 58·6; H, 3·1; N, 17·3; Cl, 21·6. $C_8H_5N_2Cl$ requires C, 58·4; H, 3·0; N, 17·0; Cl, 21·6%).

The following bromo-compounds were prepared in a similar manner to the corresponding chloro-compounds.

6-*Bromoquinoxaline*-2 : 3-*dicarboxylic acid* (VI) is moderately easily soluble in water, from which it separates in small, colourless, slender prisms containing two molecules of water which are lost at 110° (Found: loss, 11·0; Br, 24·05. $C_{10}H_5O_4N_2Br,2H_2O$ requires loss, 10·8; Br, 24·0%). The anhydrous acid melts at 172° (decomp.).

The *anhydride* (formula as III) crystallises from acetic anhydride in very pale yellow, small, flattened prisms, decomp. 235—245° (Found: Br, 28·6. $C_{10}H_3O_3N_2Br$ requires Br, 28·7%).

The *ethyl hydrogen* ester is very easily soluble in alcohol, from which it separates in very small, colourless, compact, rhombic prisms, m. p. 161° (Found: Br, 24·5. $C_{12}H_9O_4N_2Br$ requires Br, 24·6%). The *ethyl* ester is moderately easily soluble in 25% aqueous alcohol, from which it separates in colourless, long, flattened prisms, m. p. 69° (Found: Br, 22·5. $C_{14}H_{13}O_4N_2Br$ requires Br, 22·7%).

The *ammonium* salt is rather sparingly soluble in acetic acid, from which it separates in long, slender, colourless prisms, decomp. 235—240° (Found: Br, 23·9. $C_{10}H_{11}O_4N_4Br$ requires Br, 24·2%).

6-*Bromoquinoxaline* is easily soluble in water, from which it separates in fine colourless needles, m. p. 56° (Found: Br, 38·2. $C_8H_5N_2Br$ requires Br, 38·3%).

Oxidation of Quinoxaline-2 : 3-dicarboxylic Acid with Formation of Pyrazinetetracarboxylic Acid (VII).—A solution of 5 g. of quinoxaline-2 : 3-dicarboxylic acid dihydrate (1 mol.) in 60 c.c. of *N*-potassium hydroxide (3 mols.) was heated for 6 hours on a water-bath with 1000 c.c. of 2% potassium permanganate solution (6 mols.), manganese dioxide slowly separating. The small excess of permanganate was destroyed by a few drops of alcohol, and the solution was filtered, concentrated to about 80 c.c., and made just acid with hydrochloric acid (about 20 c.c.). *Dipotassium dihydrogen pyrazinetetracarboxylate* separated as a colourless crystalline precipitate; after being washed with boiling alcohol (to remove any trace of the acid), it crystallised from water, in which it was rather sparingly soluble, in compact, rhombic prisms (4 g.) (Found : K, 23·6. $C_8H_2O_8N_2K_2$ requires K, 23·5%).

Pyrazinetetracarboxylic acid was obtained from the acid potassium salt by crystallisation from 20% hydrochloric acid. It was recrystallised from water, in which it was easily soluble, separating in colourless, rhombic plates containing two molecules of water; the anhydrous acid melts with decomposition at 205° (Found : C, 33·2; H, 2·9; N, 9·4. Calc. for $C_8H_4O_8N_2,2H_2O$: C, 32·9; H, 2·75; N, 9·6%).

The *tetraethyl* ester was prepared by boiling 2 g. of the acid with 10 c.c. of alcohol, saturated with hydrogen chloride, for 8 hours. On addition of water, the ester separated as a colourless crystalline solid. It was recrystallised from alcohol, in which it was easily soluble, separating in long, colourless, rhombic prisms, m. p. 104° (Found : N, 7·5. $C_{16}H_{20}O_8N_2$ requires N, 7·6%).

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XCIV.—*The Stability of Complex Metallic Salts.*

By FREDERICK GEORGE MANN.

THE stability of the complex metallic salts is commonly considered to be based on the electronic structure of the metal when so co-ordinated, since the metal in its simple salts, when co-ordinating with amine molecules or further acid radicals, endeavours to increase the number of its electrons to that of the next inert gas (Lowry, *Chem. and Ind.*, 1923, **1**, 318; Sidgwick, J., 1923, **123**, 725; "The Electronic Theory of Valency," 1927, 113). If, then, it is assumed that co-ordinated amine, water, sulphide, or other molecules are bound to the metal by "semi-polar double bonds" (Lowry) or "co-ordinate links" (Sidgwick), contributing in each case 2

electrons per molecule to the metal, and that co-ordinated acid radicals are bound by *covalencies, contributing 1 electron per* monobasic radical to the metal, a reasonable explanation is afforded of the great stability of, *e.g.*, the complex salts of tervalent cobalt and rhodium and of quadrivalent platinum, all of co-ordination number 6. For instance, cobalt of atomic number 27 requires 9 electrons to attain the 36 electrons of krypton, and these are obtained in the hexammino-series, *e.g.*, $[Co(NH_3)_6]Cl_3$, where the metal gains $(2 \times 6) - 3 = 9$, and in the hexacido-series, *e.g.*, $Na_3[Co(NO_2)_6]$, where it again gains $(3 + 6) = 9$. Quadrivalent platinum, of atomic number 78, requires 8 electrons to equal emanation (86), and therefore gives compounds such as $[Pt(NH_3)_6]Cl_4$ and $Na_2[PtCl_6]$, in both of which the necessary electrons, $(12 - 4)$ and $(2 + 6)$, respectively, are acquired.

These considerations would explain why, for instance, the complex salts of tervalent iron are usually less stable than those of bivalent iron. Iron, of atomic number 26, requires 10 electrons to attain the 36 electrons of krypton. In potassium ferrocyanide, $K_4[FeCy_6]$, these are acquired $(4 + 6)$, but in the ferricyanide, $K_3[FeCy_6]$, the co-ordinated metal is still one short $(3 + 6)$. This deficiency is presumably the cause of the comparative instability of the ferri-complex salts. Werner prepared and resolved the chemically stable tris-$\alpha\alpha'$-dipyridylferrous bromide, $[Fe''(Dpy)_3]Br_2$ (*Ber.*, 1912, **45**, 433): on the other hand, the trisethylenediamine-ferric salts, $[Fe''' en_3]Cl_3$, are extremely unstable, and the ferri-oxalates, $Na_3[Fe(C_2O_4)_3]$, merely on exposure to light break down to the corresponding ferro-oxalates (Thomas, J., 1921, **119**, 1140).

There are, however, various metals that give at least two series of complex salts, in one of which the co-ordinated metal has a deficiency, and in the other an excess, of electrons compared with the next inert gas. It is usually found in such cases that the *metal can tolerate a deficiency of electrons more readily than an* excess, and that the series of salts having an excess of electrons is the least stable of all, usually readily reverting to a lower series by the loss of co-ordinated addenda. For instance, nickel of atomic number 28, requires 8 electrons to attain the number of krypton. In the tetrammino-series, *e.g.*, $[Ni(NH_3)_4]Cl_2$, the metal gains only 6, *i.e.*, $(8 - 2)$, and has thus a deficiency of 2 electrons; in the hexammino-series, *e.g.*, $[Ni(NH_3)_6]Cl_2$, the metal gains 10, *i.e.*, $(12 - 2)$, and has an excess of 2: salts of the hexammino-series are generally much less stable than those of the tetrammino-series, and usually revert easily to the latter in aqueous solution. Again, copper, of atomic number 29, requires similarly 7 electrons. In the tetrammino-series, *e.g.*, $[Cu(NH_3)_4]Cl_2$, it has a deficiency

1 electron, and in the hexammino-series, *e.g.*, $[Cu(NH_3)_6]Cl_2$, an excess of 3 : the latter series is much less stable than the former.

It has recently been shown, however, by the author (J., 1928, 893) that the stability of salts containing polyamines or other "multidentate" molecules is also dependent on a second factor, *viz.*, the ease with which the polyamine molecule, for purely structural reasons, can arrange itself around a complex which may be a square or tetrahedron, an octahedron, or a cube according as the metal has a co-ordination number of 4, 6, or 8, respectively. This factor, dependent on the molecular structure of the co-ordinating addendum, may have a greater effect on the stability of the complex salt than the former factor, which is dependent on the electronic structure of the metal itself.

This is well illustrated in the complex metallic salts of αβγ-triaminopropane. There is considerable evidence to show that this triamine can arrange itself readily and very firmly around the 6-co-ordination octahedron (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 80; J., 1926, 2675), and thus gives extremely stable salts such as bistriaminopropanecobaltic chloride,

$$[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Co]Cl_3,$$

and the corresponding bistriaminopropanerhodium trichloride. When, however, nickel chloride is treated with triaminopropane in any proportion, the bistriaminopropanenickelous salt, *e.g.*, $[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Ni]I_2$, is always formed. Here the metal, of co-ordination number 6, has an excess of 2 electrons, and the salt should therefore be very unstable : actually it is extremely stable, and shows no sign of degradation to a salt of co-ordination number 4, such, *e.g.*, as monoaquotriaminopropanenickelous iodide, $[H_2O\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}Ni]I_2$. Again, bivalent platinum has the characteristic co-ordination number of 4, *e.g.*, $[Pt(NH_3)_4]Cl_2$, and in this series the metal has a deficiency of 2 electrons. It has been shown, however (Mann, J., 1928, 890), that with triaminopropane, bivalent platinum gives salts such as bistriaminopropaneplatinous iodide, $[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Pt]I_2$: these are the only salts known in which bivalent platinum has a co-ordination number of 6, and, since the metal has an excess of 2 electrons, they should be very unstable. Actually they are remarkably stable, and can be recrystallised repeatedly from boiling water. The stability of these nickel and platinous salts is therefore to be attributed primarily to the ease with which the triaminopropane molecule can co-ordinate around the octahedron : the metal in each case has adopted the exceptional co-ordination number of 6 in order to provide the octahedron necessary for maximum stability of the completed complex salt.

The possibility that in salts of this type the metal has a co-ordination number of 4, and not of 6, being bound to only two of the three amino-groups in each molecule of the base, has already been discussed and disproved (Mann, *loc. cit.*, p. 893). When such salts separate from aqueous solution, each of the free and unco-ordinated amino-groups would almost undoubtedly add on a molecule of water to give a substituted ammonium hydroxide. Moreover, such salts, on treatment in solution with an excess of picric acid, should give a tetrapicrate, since in addition to the complex forming a dipicrate, each free amino-group would also combine with a molecule of picric acid. It has been shown, however, that when, *e.g.*, *bistriaminopropaneplatinous iodide* is treated with picric acid, a *dipicrate* alone results, showing conclusively that all six amino-groups are co-ordinated to the metal.

Further evidence of the stability of this 6-co-ordination grouping has now been obtained by investigating the complex salts of triaminopropane with other bivalent metals. Zinc, of atomic number 30, requires 6 electrons to attain the number in krypton. In the tetrammino-series, *e.g.*, $[Zn(NH_3)_4]Cl_2$, these are obtained (8 — 2) and the salts of this series are of moderate stability. In the hexammino-series, *e.g.*, $[Zn(NH_3)_6]Cl_2$, the metal has an excess of 4 electrons, and the salt is in consequence extremely unstable; in fact, it exists only in the solid state, and even on exposure to air loses ammonia, reverting to a salt of the lower series. With triaminopropane, however, zinc readily unites to give salts such as *bistriaminopropanezinc iodide*,

$$[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Zn]I_2:$$

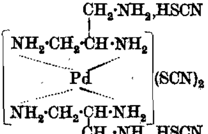
here again the metal has a co-ordination number of 6 and an excess of 4 electrons, yet the salt is extremely stable and, like the above nickelous and platinous salts, can be recrystallised repeatedly from boiling water without change.

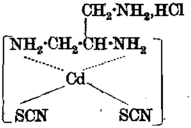
The reactions of bivalent palladium with the triamine are (as might be expected) precisely similar to those of bivalent platinum. Palladium, of atomic number 46, requires 8 electrons to attain the state of xenon. The quadrivalent metal has a co-ordination number of 6, and in compounds such as $[Pd(NH_3)_6]Cl_4$ acquires the requisite 8 electrons (6 × 2 — 4). The bivalent metal has, like platinum, the characteristic co-ordination number 4, and in compounds such as $[Pd(NH_3)_4]Cl_2$ has therefore a deficiency of 2 electrons. With triaminopropane, however, it gives compounds such as *bistriaminopropanepalladous iodide*, $[\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2Pd]I_2$: here the bivalent metal has a co-ordination number of 6, and an excess of 2 electrons, yet in spite of the latter factor the salt is very stable. These compounds, again, are the only known derivati

of bivalent palladium in which the metal shows a co-ordination number of 6.

It follows, therefore, that bivalent nickel, zinc, platinum, and palladium give complex salts with triaminopropane in all of which the metal shows the unusual (and, for the last two metals, quite abnormal) co-ordination number of 6. In each case, the co-ordinated metal has electrons in excess of the number in the next inert gas—a condition normally causing considerable instability. Actually, all these salts possess great stability, due presumably to the very firm attachment of the triamine molecule around the 6-co-ordination octahedron, a factor outweighing the former in its effect on the stability of the complex salt.

Bivalent palladium also unites with the triamine to give *bis(triaminopropane-monothiocyanate)palladous dithiocyanate* (I), in which the metal has its normal co-ordination number of 4 and each molecule of the triamine is co-ordinated by only two of its three amino-groups, the third group being free to form a salt with further hydrogen thiocyanate. This compound is identical in type with the platinous salt already described (*loc. cit.*, p. 892), and its stereochemistry has been fully described.

(I.) 


(II.)

Cadmium, however, does not behave like the above four bivalent metals, inasmuch as it, like bivalent copper, shows a co-ordination number of 4 in all its complex salts with triaminopropane. For instance, it forms a series of salts such as *tetrakistriaminopropanetriscadmium hexaiodide*, $[\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_4Cd_3]I_6$, identical in type with the cupric salts already described (J., 1926, 2682). These salts are unstable, and on being warmed with water readily lose part of the base to give very stable and slightly soluble salts such as *monoiodotriaminopropanecadmium monoiodide*,

$$[I\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}Cd]I.$$

The metal also gives salts such as *dithiocyanato(triaminopropanemonohydrochloride)cadmium* (II). This salt, like the corresponding platinous salt (J., 1928, 890), contains an asymmetric β-carbon atom, and should therefore be resolvable into optically active forms. Since it tends to lose hydrogen chloride, however, giving the very stable *monothiocyanatotriaminopropanecadmium monothio-*

cyanate, $[SCN\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}Cd]SCN$, its resolution was not attempted.

A further example of the stability of the complex salts of certain polyamines is furnished by ββ′β″-triaminotriethylamine, $N(C_2H_4\cdot NH_2)_3$. Mann and Pope showed (J., 1926, 482) that this tetramine combines with nickel salts to give tristriaminotriethylaminebisnickelous *tetraiodide*, $[\{N(C_2H_4\cdot NH_2)_3\}_3Ni_2]I_4$. Here, again, the nickel has a co-ordination number of 6, and an excess of 2 electrons, yet this salt and the corresponding tetrabromide are extremely stable and may be recrystallised repeatedly from boiling water without change.

EXPERIMENTAL.

In the following formulæ, the symbol "ptn" represents one molecule of αβγ-triaminopropane.

Bistriaminopropanezinc Iodide, $[Zn\,ptn_2]I_2$.—Triaminopropane trihydrochloride (6·6 g.; 3 mols.), dissolved in 15% sodium hydroxide solution (24 c.c.), is added with stirring to a solution of zinc nitrate (3 g.) in water (40 c.c.). The white precipitate which is first formed rapidly redissolves, and the clear solution is concentrated on the water-bath, chilled, and filtered. The addition of concentrated potassium iodide solution gives a crystalline precipitate, which, when recrystallised from water, gives the above *iodide* as fine white crystals; these have no melting point, but decompose slowly between 255° and 270° (Fonnd: C, 14·6; H, 4·5; I, 50·6. $C_6H_{22}N_6I_2Zn$ requires C, 14·5; H, 4·4; I, 51·0%).

Bistriaminopropanepalladous Iodide, $[Pd\,ptn_2]I_2$.—A solution of ammonium chloropalladite (15 g.) in water (200 c.c.) is slowly added to a solution of triaminopropane trihydrochloride (34·5 g. 3 mols.) in 15% sodium hydroxide solution (127 c.c.); the whitish yellow precipitate produced rapidly redissolves. The clear solution is concentrated on the water-bath, much ammonia being given off, and is then chilled and treated with saturated potassium iodide solution, a fine white powder being steadily deposited: after 2 hours, this is collected, and recrystallised three times from hot water to eliminate traces of potassium iodide. The above *iodide* is thus obtained as a fine, white, crystalline powder, m. p. 23[illegible] (decomp.), freely soluble in cold water (Found: C, 13·3; H, 4·[illegible] I, 46·9; Pd, 20·0. $C_6H_{22}N_6I_2Pd$ requires C, 13·3; H, 4·1; [illegible] 47·1; Pd, 19·8%).

Bis(triaminopropane-monothiocyanate)palladous Dithiocyanate ([illegible] —The clear concentrated solution obtained in the preparation of the above iodide is treated with a concentrated solution of potassium thi[illegible] [illegible] containing free acetic acid. A voluminous white precipita[illegible]

slowly separates: this is recrystallised three times from hot water, the solid product being each time thoroughly drained by suction to remove the last trace of potassium thiocyanate solution, which is held very tenaciously by the crystalline substance. The *dithiocyanate* is obtained as a fine white crystalline powder, m. p. 166—168° (decomp.), freely soluble in water (Found: C, 22·9; H, 4·7; N, 27·3; Pd, 20·5; SCN, 44·5. $C_{10}H_{24}N_{10}S_4Pd$ requires C, 23·1; H, 4·7; N, 27·0; Pd, 20·6; 4SCN, 44·7%).

Tetrakistriaminopropanetriscadmium Hexaiodide, $[Cd_3\,ptn_4]I_6$.—A solution of hydrated cadmium chloride (4 g.) in water (20 c.c.) is slowly added to a solution of triaminopropane trihydrochloride (12 g.; 3 mols.) in 15% sodium hydroxide solution (44·4 c.c.). The white precipitate formed rapidly redissolves, and the clear solution, after 1 hour, is treated with saturated potassium iodide solution. The heavy white crystals which slowly separate are washed with much cold water and dried in a vacuum over sulphuric acid (Found: C, 9·9; H, 3·3; N, 11·6; I, 52·2. $C_{12}H_{44}N_{12}I_6Cd_3$ requires C, 9·9; H, 3·1; N, 11·6; I, 52·35%). The crystalline *hexaiodide* is only slightly soluble in cold water, in which it is quite stable: boiling water, however, converts it into the monoiodide described below.

The corresponding *hexabromide*, $[Cd_3\,ptn_4]Br_6,3H_2O$, is prepared by treating the clear solution, obtained in the preparation of the above hexaiodide, with saturated sodium bromide solution. The white crystals of the hexabromide separate very slowly in the course of several days: they are washed with cold water and dried (Found: N, 13·7; Br, 39·1. $C_{12}H_{44}N_{12}Br_6Cd_3,3H_2O$ requires N, 13·7; Br, 39·1%).

Monoiodotriaminopropanecadmium monoiodide, [I ptn Cd]I, is obtained by adding the above hexaiodide to much boiling water. The clear solution is rapidly filtered, and the monoiodide separates in large white crystals, m. p. 210—213°, only slightly soluble in boiling water (Found: C, 7·9; H, 2·5; N, 9·3; I, 55·8. $C_3H_{11}N_3I_2Cd$ requires C, 7·9; H, 2·4; N, 9·2; I, 55·7%).

Monobromotriaminopropanecadmium monobromide, [Br ptn Cd]Br, is obtained similarly by treating the hexabromide with boiling water, and separates as white crystals, m. p. 221—223° (decomp.) (Found: C, 9·9; H, 3·35; N, 11·6; Br, 44·3. $C_3H_{11}N_3Br_2Cd$ requires C, 10·0; H, 3·1; N, 11·6; Br, 44·2%).

Monothiocyanatotriaminopropanecadmium Monothiocyanate, [SCN ptn Cd]SCN.—If the clear solution obtained by treating the base with cadmium chloride (as in the preparation of the hexaiodide) is treated with potassium thiocyanate solution, no trace of a corresponding hexathiocyanate can be detected. The addition

of the potassium salt gives a white precipitate, which dissolves readily in excess of thiocyanate. The clear solution obtained slowly deposits large white crystals of the above *monothiocyanate*: these are almost insoluble in cold water, and only slightly soluble in boiling water, from which they crystallise unchanged in composition, and of m. p. 201—202° (decomp.) (Found: for the crude material, N, 22·3; for the recrystallised material, N, 22·1; S, 20·1. $C_5H_{11}N_5S_2Cd$ requires N, 22·1; S, 20·2%). This compound is extremely stable, and in the estimation of sulphur by Carius's method the heating with nitric acid must be continued for 12 hours at 260° to ensure conversion of all the sulphur into sulphuric acid.

Dithiocyanato(triaminopropane-monohydrochloride)cadmium (II).—The clear solution obtained as before is treated with potassium thiocyanate solution containing free acetic acid. Large colourless crystals slowly separate: after 24 hours, these are collected and recrystallised twice from hot water. The *compound* is thus obtained as fine white crystals, m. p. 150—154° (decomp.), moderately easily soluble in water: if the hot aqueous solution is cooled too rapidly, the compound separates as an oil (Found: C, 17·0; H, 3·4; N, 19·9; SCN + Cl, 42·5. $C_5H_{12}N_5ClS_2Cd$ requires C, 17·0; H, 3·4; N, 19·8; 2SCN + Cl, 42·8%). The compound on exposure to air slowly loses hydrogen chloride, apparently with the formation of the monothiocyanate described above.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.
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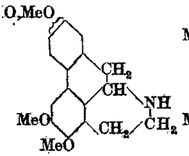
XCV.—*Synthetical Experiments on the Aporphine Alkaloids. Part V. Laurotetanine. Syntheses of 2 : 3 : 6 : 7- and 3 : 4 : 6 : 7-Tetramethoxyaporphines.*

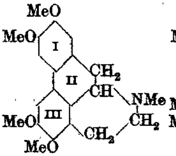
By ROBERT KENNETH CALLOW, JOHN MASSON GULLAND, and ROBERT DOWNS HAWORTH.

GORTER (*Bull. Jard. bot. Buitenzorg*, 1921, [iii], 3, 180) assigne the constitution (I) to laurotetanine, an aporphine alkaloid whic causes tetanic convulsions when injected. It has been isolat from the bark of various *Lauraceæ*, particularly from *Litsea* speci native to Java (Greshoff, "Verslag v.h. onderzoek v.d. Plante stoffen Ned. Indie," 1890, 98; *Ber.*, 1890, 23, 3537; Filippo, *Ar Pharm.*, 1898, 236, 601). Gorter prepared from laurotetanine substance which he regarded as the dimethyl derivative, a ... The similarity in chemical and physiologi

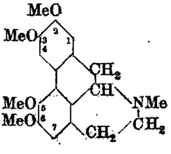
properties of *iso*glaucine and glaucine (III) (Gadamer, *Arch. Pharm.*, 1911, **249**, 680) suggested to Gorter that the two bases must contain the same carbon skeleton, and he assigned the constitution (II) to *iso*glaucine. The positions of the oxygen atoms in this structure were deduced from two considerations. In the first place, the oxidation of laurotetanine by alkaline permanganate yielded 1 : 2-dimethoxybenzene-3 : 4 : 5-tricarboxylic acid, thus establishing the relative positions of the methoxy-groups in ring III. This acid might be obtained with equal ease from the base (I), where the methoxyls are in the 6 : 7-positions, or from a substance of the nature of glaucine, in which the methoxyls are in the 5 : 6-positions, and Gorter based his choice of the 6 : 7-positions on the fact that *iso*glaucine appeared to differ both from glaucine and from corytuberine dimethyl ether (III, but with methoxyls in the 3 : 4-positions). Secondly, the close similarity of the colour reactions exhibited by *iso*glaucine with those shown by glaucine convinced Gorter that the arrangement of the methoxyl groups in ring I was that present in glaucine.



(I.)



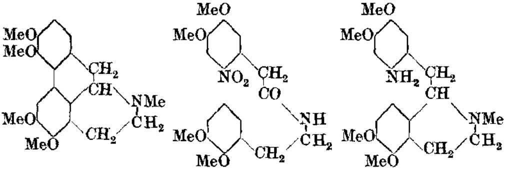
(II.)



(III.)

The recent investigations of Barger and Silberschmidt (*J.*, 1928, 2919) and of Späth and Strauhal (*Ber.*, 1928, **61**, 2395) have shown that *iso*glaucine was in reality impure glaucine, and therefore did not contain the vicinal homocatechol group in ring III. Some time before the appearance of these results, theoretical considerations had convinced us that this vicinal arrangement does not occur in the aporphine series, and it then became evident that syntheses of 2 : 3 : 6 : 7-tetramethoxyaporphine (II) and of 3 : 4 : 6 : 7-tetramethoxyaporphine (IV) would be of great value in elucidating the true nature of laurotetanine. The inclusion of the base (IV) as a possible structure of *iso*glaucine was the result of a comprehensive comparison of the colour reactions of the aporphines (p. 669) which made it evident that the colours developed by the base (II) need not necessarily be those exhibited by glaucine, and consequently that reliance could not be placed on Gorter's assumption as to the position of the oxygen atoms in ring I. 2 : 3 : 6 : 7-Tetra

methoxyaporphine and 3 : 4 : 6 : 7-tetramethoxyaporphine have therefore been prepared synthetically. As is to be expected in the light of the work of Barger and of Späth, neither substance resembles *iso*glaucine.



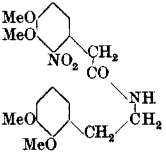
(IV.) (V.) (VI.)

6-Nitro-3 : 4-dimethoxyphenylacetic acid was prepared both by the nitration of 3 : 4-dimethoxyphenylacetic acid, and also from 6-nitrohomoveratrole by a modification of the method of Oxford and Raper (J., 1927, 417). β-2 : 3-Dimethoxyphenylethylamine was obtained as described by Haworth (J., 1927, 2282) from β-2 : 3-dimethoxyphenylpropionic acid (Perkin and Robinson, J., 1914, **105**, 2387) and the corresponding amide. The last substance was also prepared from methyl β-2 : 3-dimethoxyphenylpropionate by the action of concentrated ammonia solution.

Some difficulty was experienced in preparing *6′-nitro-3′ : 4′-dimethoxyphenylaceto-β-2 : 3-dimethoxyphenylethylamide* (V), owing to the instability of 6-nitro-3 : 4-dimethoxyphenylacetyl chloride. Since this behaviour is unlike that of 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (Part II, J., 1928, 1132), it would seem that this is an example of the greatly enhanced reactivity of the methyl group of 6-nitrohomoveratrole derivatives as compared with those of 2-nitrohomoveratrole (compare Part I, J., 1928, 581), and that the formation of 6-nitro-3 : 4-dimethoxyphenylacetyl chloride is followed by the interaction of the carboxyl chloride with the activated methylene group of another molecule. Yet a further example of this difference in activity was observed during an attempt to prepare the amide (V) by heating a mixture of 6-nitro-3 : 4-dimethoxyphenylacetic acid and β-2 : 3-dimethoxyphenylethylamine. At about 130°, carbon dioxide was smoothly evolved, and pure 6-nitrohomoveratrole remained in theoretical yield. In a parallel experiment, no reaction took place between 2-nitro-3 : 4-dimethoxyphenylacetic acid and β-2 : 3-dimethoxyphenylethylamine below 175°, and when the temperature was raised above this point no homogeneous material could be isolated. Ultimately, the amide (V) was obtained by adding a chloroform solution of the acid

chloride (prepared by means of phosphorus pentachloride, and containing phosphorus oxychloride) to a mixture of a chloroform solution of β-2 : 3-dimethoxyphenylethylamine and a dilute aqueous solution of sodium hydroxide.

The action of phosphorus pentachloride in cold chloroform solution converted the amide (V) into *6′-nitro-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-3 : 4-dihydroisoquinoline*. The *methiodide* of this base was reduced by means of zinc dust and hydrochloric acid to *6′-amino-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline* (VI), which was isolated as the crystalline *dihydrochloride*, and yielded dl-2 : 3 : 6 : *7-tetramethoxyaporphine* (II) when diazotised in methyl-alcoholic sulphuric acid. Attempts to resolve this base by means of *d*- and *l*-tartaric acids were unsuccessful. The colours developed with sulphuric acid, nitric acid, Mandelin's, Fröhde's, and Erdmann's reagents did not resemble those described by Gorter for *iso*glaucine.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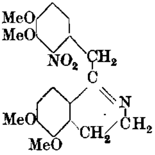
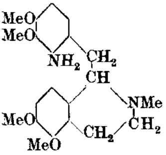

(VIII.)


(IX.)

2′-Nitro-3′ : 4′-dimethoxyphenylaceto-β-2 : 3-dimethoxyphenylethylamide (VII), prepared by the interaction of 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (Part II, J., 1928, 1132) with β-2 : 3-dimethoxyphenylethylamine, yielded *2′-nitro-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-3 : 4-dihydroisoquinoline* (VIII) when submitted to the action of phosphorus pentachloride in cold chloroform solution. The reduction of the *methiodide* of this base by means of zinc dust and hydrochloric acid produced crystalline *2′-amino-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-2-methyltetrahydroisoquinoline* (IX), which was converted into dl-3 : 4 : 6 : *7-tetramethoxyaporphine* (IV) by diazotisation in methyl-alcoholic sulphuric acid. This *dl*-base was purified by conversion into the crystalline *hydriodide* and, after being regenerated from this salt, crystallised readily from ligroin. The resolution of the *dl*-base by means of *d*- and *l*-tartaric acids yielded d-3 : 4 : 6 : *7-tetramethoxyaporphine hydrogen* d-*tartrate* and l-3 : 4 : 6 : *7-tetramethoxyaporphine hydrogen* l-*tartrate* in crystalline condition, and from these salts were isolated d-3 : 4 : 6 : *7-tetramethoxyaporphine*, m. p. 125—125·5°, $[\alpha]_D^{20°}$ 168°, and l-3 : 4 : 6 : 7-

tetramethoxyaporphine, m. p. 125·5—126°, $[\alpha]_D^{20°}$ − 167°. The crystalline *methiodide* was readily obtained by heating the *l*-base with methyl iodide.

EXPERIMENTAL.

β-2 : 3-Dimethoxyphenylpropionamide was obtained in 95% of the theoretical yield by the interaction of the acid chloride with ammonia (Haworth, *loc. cit.*), and also, in lower yield, by the interaction of the methyl ester with ammonia. β-2 : 3-Dimethoxyphenylpropionic acid (35 g.) was heated under reflux for 3 hours with an excess of methyl alcohol containing hydrogen chloride. The liquid was poured into brine, and the oily ester completely extracted with sodium carbonate, dried, and distilled, finally under reduced pressure. Methyl β-2 : 3-dimethoxyphenylpropionate passed over at 166—176°/15 mm. The ester (28 g.) and concentrated aqueous ammonia (250 c.c.) were shaken together for 40 hours; the clear solution obtained yielded crystals of the amide (15·1 g.) when evaporated in an open basin to remove excess of ammonia. The amide crystallised from light petroleum in colourless needles, m. p. 98—99°, b. p. 233—235°/16 mm. It was converted into β-2 : 3-dimethoxyphenylethylamine, b. p. 158—159°/25 mm., in the manner described by Haworth (*loc. cit.*). (In the description there given, p. 2283, line 1, 33 g. should read 3·3 g.)

In the preparation of 6-nitro-3 : 4-dimethoxyphenylacetic acid by the method of Oxford and Raper (*loc. cit.*), the yield of 6-nitro-3 : 4-dimethoxyphenylpyruvic acid was improved by increasing the proportions of potassium ethoxide and ethyl oxalate to 6-nitrohomoveratrole. The quantities used by Oxford and Raper for 50 g. of 6-nitrohomoveratrole were used for 41 g., and the yield (42 g.) rose from 60% to 77% of the theoretical.

The process for the conversion of the phenylpyruvic acid into the phenylacetic acid was also modified. "Perhydrol" was slowly added to an ice-cold solution of 6-nitro-3 : 4-dimethoxyphenylpyruvic acid (42 g.) in 2*N*-sodium hydroxide (300 c.c.) until the violet colour was discharged. A small quantity of white slimy material was removed, and acidification of the filtrate with dilute sulphuric acid yielded 6-nitro-3 : 4-dimethoxyphenylacetic acid, m. p. 203—204° (31 g.; 83% of the theoretical yield). When crystallised from alcohol, this acid formed brown needles, m. p. 206—207°.

The preparation of 6-nitro-3 : 4-dimethoxyphenylacetic acid by nitration was performed as follows: A mixture of 3 : 4-dimethoxyphenylacetic acid (36 g.) and glacial acetic acid (80 c.c.) was stirred mechanically and cooled in ice. Fuming nitric acid (24 c.c.) in

acetic acid (20 c.c.) was added slowly, and the mixture poured into water. The precipitated acid was dried; it crystallised from glacial acetic acid in faintly yellow needles, m. p. 206—207°, or from ethyl acetate in colourless needles having the same melting point (Found: C, 50·0; H, 4·8. Calc. for $C_{10}H_{11}O_6N$: C, 49·8; H, 4·6%). It was very sparingly soluble in benzene, chloroform, and cold water, and sparingly soluble in glacial acetic acid and ethyl acetate. Oxford and Raper record the melting point as 202—204°, and state that the acid is readily soluble in glacial acetic acid and in ethyl acetate. The specimen prepared by their method was identical in every respect with that just described.

6′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide* (V).—Preliminary experiments showed that 6-nitro-3 : 4-dimethoxyphenylacetyl chloride could not be prepared in the same way as the 2-nitro-derivative. When the mixture of the acid with thionyl chloride in benzene was gently warmed, decomposition occurred, accompanied by blackening, and no crystalline amide could be prepared from the product obtained after removal of thionyl chloride. The chloride appeared to be formed when slightly more than one molecular proportion of phosphorus pentachloride was added to a suspension of the acid in chloroform. Heating or the addition of pyridine to this solution caused decomposition, since the liquid darkened considerably, and no amide could be separated from the tarry product obtained after the addition of β-2 : 3-dimethoxyphenylethylamine and treatment in the usual way. Some of the desired product was obtained, however, by the addition of an excess of the amine to the solution containing the acid chloride, and finally the following process was adopted. The acid (13·1 g.) was suspended in dry chloroform, and phosphorus pentachloride (25 g.) gradually added. After being shaken for 20 minutes, all the phosphorus pentachloride and acid had passed into solution, and the liquid was then added slowly to a vigorously stirred mixture of the amine (12 g.) in chloroform (50 c.c.) and dilute aqueous sodium hydroxide (250 c.c. of 2*N*-solution and 400 c.c. of water) which was cooled in ice. After about 20 minutes, the chloroform was separated, the aqueous layer extracted with chloroform, and the combined chloroform solutions were washed with dilute acid, dried, and evaporated. The residual gum was dissolved in hot methyl alcohol, and on cooling, the product separated in colourless needles (9·5 g.). When recrystallised from methyl alcohol and from benzene, 6′-*nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide* separated as needles, m. p. 144·5—145·5° (Found: C, 59·8; H, 6·2. $C_{20}H_{24}O_7N_2$ requires C, 59·4; H, 5·9%).

6′-*Nitro*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline*.

—A mixture of the amide (9·5 g.) and a solution of phosphorus pentachloride (11 g.) in chloroform (60 c.c.) was kept in a closed vessel. Separation of nodular crystals began after 3 days and appeared to be complete after 4 days. The mixture was poured into dilute hydrochloric acid, the chloroform evaporated by heating, and the residual tar removed by filtration. When the filtrate was made alkaline with ammonia, a tar was precipitated which soon solidified (6 g.). After crystallisation from methyl alcohol, in which it was sparingly soluble, and from benzene, in which it dissolved rather readily, *6′-nitro-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline* was obtained as colourless prisms, m. p. 187·5—189·5° (Found : C, 62·2 ; H, 5·9. $C_{20}H_{22}O_6N_2$ requires C, 62·2 ; H, 5·7%). This substance melted to a deep red liquid, and the colour faded on resolidification. The formation of the *iso*quinoline was incomplete, since the tar which was insoluble in hydrochloric acid yielded 1·0 g. of unchanged amide on treatment with methyl alcohol.

The *methiodide* was prepared by heating the base (3·1 g.) with purified methyl iodide under reflux for 12 hours, and separated as yellow crystals (4·95 g.), m. p. 111° (decomp. with effervescence) Good analytical figures could not be obtained for this substance When recrystallised from absolute alcohol, it separated as an oil which solidified only when rubbed. This solid, m. p. 146—147 (with decomposition to a red liquid, after softening at 140°), wa dried in a vacuum (Found : C, 50·2 ; H, 5·3. $C_{21}H_{25}O_6N_2I$ require C, 47·7 ; H, 4·7%). The solution in alcohol was red, and whe crystallisation took place slowly in a not too concentrated solutio a mixture of yellow and red crystals separated, m. p. 115—124 (decomp.). An apparently homogeneous product was slowly pr cipitated as a yellow powder, m. p. 146—148° (decomp. ; softenin at 140°), when an excess of benzene was added to a solution of th methiodide in absolute alcohol (Found : C, 49·6 ; H, 5·4%). Th analytical figures do not correspond to any simple addition solvent. When heated at 100°, the substance darkened slowly an the m. p. fell to 108—120° (decomp. at 137°). The addition ammonia to an aqueous solution of the methiodide precipitat reddish-purple flocks. These formed a bright red solution benzene (compare the behaviour of the 2′-nitro-derivative, p. 66 and were probably 6′-nitro-3′ : 4′ : 5 : 6-tetramethoxy-1-benz idene-2-methyltetrahydro*iso*quinoline, since the methiodide w regenerated by the action of hydriodic acid.

*6′-Amino-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-2-methyl-1 : 2 : 3 : tetrahydro*iso*quinoline* (VI).—The methiodide (3·5 g.) was suspend in a mixture of concentrated hydrochloric acid (80 c.c.) and wa

(35 c.c.), heated on the water-bath, and zinc dust (25 g.) added slowly until the solution was decolorised. The filtered solution was basified with an excess of ammonia, and the mixture extracted thoroughly with ether. Evaporation of the ethereal solution yielded a gum, which could not be induced to crystallise and was therefore dissolved in chloroform and converted into the dihydrochloride by means of hydrogen chloride. The addition of ether precipitated a copious white solid (2·2 g.). When purified by two recrystallisations from absolute alcohol, 6′-*amino*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline dihydrochloride* formed microscopic short needles, m. p. 233·5—235° (decomp.) (Found: C, 56·7; H, 6·8. $C_{21}H_{28}O_4N_2$,2HCl requires C, 56·6; H, 6·8%). The addition of sodium nitrite to the solution in dilute hydrochloric acid caused the development of a deep blue coloration, which faded in a few minutes through blue-green to yellow. A red precipitate of an azo-dye was obtained when this solution was added to an alkaline solution of β-naphthol.

dl-2 : 3 : 6 : 7-*Tetramethoxyaporphine* (II).—A solution of the preceding dihydrochloride (1·94 g.) in a mixture of methyl alcohol (10 c.c.) and 2*N*-sulphuric acid (10 c.c.) cooled in a freezing mixture was diazotised with the calculated quantity of sodium nitrite solution. After being kept at the ordinary temperature for 2 hours, the solution was boiled under reflux for 1 hour, concentrated hydrochloric acid (3 c.c.) added, and the mixture reduced by the gradual addition of zinc dust (1 g.). From the filtered solution, rendered alkaline with an excess of sodium hydroxide, ether extracted a gum. This was dissolved in dilute hydrochloric acid, an excess of sodium iodide added, the supernatant liquid poured off, and the precipitated gum stirred with alcohol; the crude hydriodide, thus obtained as a white powder (0·55 g.), melted at 227·5—230·5° (decomp.; after darkening above 200°). When the hydriodide was ground with sodium hydroxide solution, a brown viscous oil was formed; this was extracted with chloroform, and the extract dried and evaporated. dl-2 : 3 : 6 : 7-*Tetramethoxyaporphine*, m. p. 115·5—116·5°, was obtained in very pale yellow nodules from the gummy residue by repeated recrystallisation from light petroleum (b. p. 60—80°) (Found, by microanalysis: C, 71·0; H, 6·9. $C_{21}H_{25}O_4N$ requires C, 71·0; H, 7·0%). The methiodide, obtained as a colourless solid when the base was warmed with a little alcohol and excess of methyl iodide, was freed from solvent by heating on the water-bath; it crystallised from much methyl alcohol in needles, m. p. 204—208°.

An attempt was made to resolve the *dl*-base by forming the hydrogen *d*-tartrate, but this could only be obtained as a gum.

By a fractional separation from absolute alcohol, and the conversion of the more soluble fraction into the hydrogen *l*-tartrate, a second gum was obtained which did not become crystalline by repeated separations from absolute alcohol. Both yielded the unchanged base, m. p. 115·5—116·5°, which showed no evidence of optical activity.

The following colour reactions were given by the *dl*-base :

Concentrated sulphuric acid :	Emerald-green, becoming intensely green on warming, and red on dilution.
Concentrated nitric acid :	Indigo, becoming deep purple and finally brown on warming.
Fröbde's reagent :	Colourless.
Erdmann's reagent :	Deep reddish-purple.
Mandelin's reagent :	Transient green, becoming reddish-purple and finally brown.

2′-Nitro-3′ : 4′-dimethoxyphenylaceto-β-2 : 3-dimethoxyphenylethylamide (VII).—To a cooled solution of β-2 : 3-dimethoxyphenylethylamine (14 g.) in dry benzene (30 c.c.), a solution of 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (from 19 g. of the acid) in dry benzene (70 c.c.) was slowly added, followed by a slight excess of 2*N*-sodium hydroxide. The benzene layer was separated, the aqueous layer again extracted with benzene, and the combined extracts washed with dilute acid and with water and evaporated. The tarry residue was with some difficulty induced to crystallise by rubbing with methyl alcohol (yield, 26 g. ; m. p. 81—89°). After recrystallisation from a small quantity of methyl alcohol and from 60% ethyl alcohol, *2′-nitro-3′ : 4′-dimethoxyphenylaceto-β-2 : 3-dimethoxyphenylethylamide* was obtained as colourless needles, m. p. 95—96° (Found : N, 6·7. $C_{20}H_{24}O_7N_2$ requires N, 6·9%). It was very soluble in benzene, readily soluble in methyl or ethyl alcohol, fairly soluble in carbon tetrachloride, and insoluble in light petroleum.

*2′-Nitro-3′ : 4′ : 5 : 6-tetramethoxy-1-benzyl-3 : 4-dihydro*isoquinoline (VIII).—The amide (4·5 g.) was mixed with phosphorus pentachloride (5 g.) in chloroform suspension (30 c.c.) and kept in a closed vessel. After 36 hours a mass of nodular crystals had separated. These appeared to consist of an additive compound of the product and phosphorus pentachloride or phosphoryl chloride, since a portion of the solid, when separated and washed with chloroform, was highly hygroscopic, and the solution in water gave strong positive reactions for both phosphate and chloride. The reaction mixture was poured into water, the chloroform evaporated on the water-bath, and the solution filtered from the residual tar. The addition of an excess of ammonia yielded a gummy precipitate which soon solidified (2·5 g.). When recrystallised twice from

methyl alcohol, *2'-nitro-3' : 4' : 5 : 6-tetramethoxy-1-benzyl-3 : 4-dihydroisoquinoline* was obtained as peach-coloured prisms, melting at 152—156° to a red liquid (Found : C, 62·4; H, 5·7. $C_{20}H_{22}O_6N_2$ requires C, 62·2; H, 5·7%).

The *methiodide* separated in clusters of small needles containing methyl iodide of crystallisation, m. p. 110—116° (efferv.), when a solution of the base in excess of boiling methyl iodide was allowed to cool (Found : loss at 95°, 20·3. $C_{21}H_{25}O_6N_2I,CH_3I$ requires loss, 21·2%). After drying at 95°, the methiodide melted at 183—184° (decomp.) (Found : C, 47·8; H, 5·1. $C_{21}H_{25}O_6N_2I$ requires C, 47·7; H, 4·7%). It could not be recrystallised satisfactorily, and the specimen used for analysis was prepared from the pure base. The methiodide was very soluble in methyl or ethyl alcohol and in chloroform and very sparingly soluble in carbon tetrachloride. When ammonia was added to an aqueous solution, an orange-red amorphous precipitate separated, which formed an orange solution in benzene (compare p. 664).

2'-Amino-3' : 4' : 5 : 6-tetramethoxy-1-benzyl-2-methyltetrahydroisoquinoline (IX).—The methiodide (6 g.) was suspended in a mixture of hydrochloric acid (120 c.c.) and water (80 c.c.), heated on the water-bath, and zinc dust (18 g.) added gradually until the solution was completely decolorised. The solution was filtered while hot, and basified with concentrated ammonia solution. The resulting purple solution was extracted with ether (500 c.c.), and the extract dried over sodium sulphate and evaporated to dryness. A mixture of crystals with a little gum remained (3·7 g.). An attempt to isolate the product by passing hydrogen chloride into the ethereal solution yielded a sticky product which could not be made to crystallise, and the method just described was more satisfactory. When purified by recrystallisation from ether, *2'-amino-3' : 4' : 5 : 6-tetramethoxy-1-benzyl-2-methyltetrahydroisoquinoline* was obtained as colourless rhombic plates, m. p. 117·5—119·5° (Found : C, 67·7; H, 7·4. $C_{21}H_{28}O_4N_2$ requires C, 67·7; H, 7·5%). A diazotised solution of the amine in hydrochloric acid gave with an alkaline solution of β-naphthol a scarlet azo-dye.

dl-*3 : 4 : 6 : 7-Tetramethoxyaporphine* (IV).—The preceding amine (3·72 g.) was dissolved in a mixture of ice-cold 2*N*-sulphuric acid (20 c.c.) and methyl alcohol (20 c.c.) and diazotised with the calculated amount of sodium nitrite solution. After 20 minutes, the mixture was boiled on the water-bath for ½ hour, reduced with concentrated hydrochloric acid (6 c.c.) and zinc dust (2 g.), cooled, and made strongly alkaline by the addition of sodium hydroxide. The product was only slowly extracted by ether, and a large volume (900 c.c.) was found to be necessary. The ethereal solution, when

dried over sodium sulphate and evaporated, left a gummy residue, which was dissolved in the minimum quantity of dilute hydrochloric acid and treated with an excess of sodium iodide. A gum separated; the supernatant liquid was poured off, and the gum stirred with methyl alcohol (20 c.c.). dl-3 : 4 : 6 : 7-*Tetramethoxyaporphine hydriodide* was thus obtained as a white powder, which formed long prisms from methyl alcohol, m. p. 257—262° after darkening (Found: C, 52·6; H, 5·4. $C_{21}H_{25}O_4N,HI$ requires C, 52·2; H, 5·4%). The free base was obtained by grinding the hydriodide with a slight excess of sodium hydroxide; the dried solid (0·87 g., m. p. 122—127°) was repeatedly crystallised from light petroleum, dl-3 : 4 : 6 : 7-*tetramethoxyaporphine* being obtained as clear yellow plates, m. p. 131—132° (Found, by microanalysis: C, 70·9; H, 7·2. $C_{21}H_{25}O_4N$ requires C, 71·0; H, 7·0%). The substance was very soluble in methyl and ethyl alcohols, acetone, benzene, and ether, but insoluble in water.

Resolution of dl-3 : 4 : 6 : 7-*Tetramethoxyaporphine*.—The crude base (0·7404 g.) was treated with a saturated solution of *d*-tartaric acid (1 mol.; 0·3336 g.) in absolute alcohol. No separation took place, even after some time, but a caseous precipitate (0·5 g.) was obtained by the addition of benzene to a solution in slightly aqueous alcohol. The filtrate yielded a gum (0·7 g.) when evaporated to dryness. The precipitate, after being twice recrystallised from 96% alcohol, yielded d-3 : 4 : 6 : 7-*tetramethoxyaporphine hydrogen* d-*tartrate* in bunches of needles, m. p. 174—185° after softening (Found: loss at 80° in a vacuum over P_4O_{10}, 6·4, 7·0; loss at 110° in a vacuum over P_4O_{10}, 7·3. $C_{25}H_{31}O_{10}N,2H_2O$ requires loss, 6·7%). The anhydrous salt regained water rapidly in the air. When it was heated at 110°, slight decomposition occurred, for the salt then crystallised poorly from alcohol and low values were obtained for the rotations of the salt and of the base as compared with those of the optical isomerides. Concordant values were given, however, by a specimen obtained by repeating the process of resolution. In water, the hydrogen *d*-tartrate had $[\alpha]_D^{20°}$ + 84·9° (c = 0·930). The base was liberated from the bitartrate by sodium hydroxide, and extracted with chloroform. The residue left by evaporation of the chloroform was recrystallised from light petroleum, yielding d-3 : 4 : 6 : 7-*tetramethoxyaporphine* as long, pale yellow prisms, m. p. 125—125·5°. In chloroform (c = 0·459), $[\alpha]_D^{20°}$ = + 168°.

From the mother-liquors and residues of the isolation of the *d*-base *d*-bitartrate, the basic material was liberated, and extracted with ether, and the extracts were evaporated in a weighed dish. The gum (0·4955 g.) obtained was treated with *l*-tartaric acid

(0·2235 g.) in alcohol. Crystals readily separated from the solution, and after three recrystallisations from alcohol, 1-3 : 4 : 6 : 7-*tetramethoxyaporphine hydrogen* l-*tartrate* was obtained as needles, m. p. 170—180° after softening (Found, by microanalysis: loss at 100° over P_4O_{10} in a vacuum, 7·5. Found in anhydrous material: C, 58·7; H, 6·1. $C_{25}H_{31}O_{10}N,2H_2O$ requires loss, 6·7%. $C_{25}H_{31}O_{10}N$ requires C, 58·1; H, 6·1%). In water (c = 2·044), $[\alpha]_D^{18·5°} = -85·2°$. l-3 : 4 : 6 : 7-*Tetramethoxyaporphine* was obtained from this salt, and formed long, pale yellow prisms from light petroleum, m. p. 125·5—126°. In chloroform (c = 0·978), $[\alpha]_D^{20°} = -167°$ (Found, by microanalysis: C, 70·8; H, 6·8. $C_{21}H_{25}O_4N$ requires C, 71·0; H, 7·0%).

l-3 : 4 : 6 : 7-Tetramethoxyaporphine methiodide was obtained as a white solid when the *l*-base was warmed with excess of methyl iodide. After being freed from methyl iodide by heating on the water-bath, it melted at 208—210°.

The following colour reactions were given by the *l*-base:

Concentrated sulphuric acid:	Very pale green, or blue-green in larger amount. Changed to orange-red by addition of nitric acid.
Concentrated nitric acid:	Immediate orange-red colour.
Fröhde's reagent:	Barely perceptible straw colour.
Erdmann's reagent:	Immediate deep greenish-blue, changing quickly to orange-red.
Mandelin's reagent:	Deep blue-green, changing to brown.

Colour Reactions of the Aporphines.

Aporphine.	Mandelin.	Erdmann.	Fröhde.	H_2SO_4.	HNO_3.
Glaucine	Green, blue-violet.	Blue, green-blue.	Green, blue, indigo, violet.	Nil, deep blue at 100°.	Green, deep red.
Laurotetanine	Indigo, brown, yellow.	Deep blue, brown, violet.	Indigo, brown.	Rose-red or green-blue, violet at 100°.	Red-brown.
Bulbocapnine	Blue, darker.	Blue, blue-violet.	Dark blue.	Orange, violet.	Red-brown.
Bulbocapnine methyl ether	Red, violet, blue.	Deep red.	Deep green-blue.	Nil, orange-red.	—
Corytuberine	Grey-blue, dark green.	Green, blue-violet.	Steel-blue, indigo, blue-green.	Nil, green, red, violet.	Blood-red.
Corytuberine dimethyl ether	Pale red, green, olive.	Nil, bright green.	Nil, moss-green.	Nil.	Instant blood-red.
Corydine	Transient violet, green.	Emerald.	Malachite-green.	Nil.	Blood-red.
*iso*Corydine	Violet.	Pale yellow, green.	Pale violet, green-brown.	Nil.	Red-brown.
Dicentrine	Deep blue.	Nil, soon blue.	Deep blue, green-blue, violet.	Nil, soon violet-red.	Nil, blue-green, yellow, brown.
*epi*Dicentrine	—	—	—	Red-violet.	Blue-green.
Domesticine and *iso*-D.	—	—	—	—	Blue.

Aporphine.	Mandelin.	Erdmann.	Fröhde.	H_2SO_4.	HNO_3.
5 : 6-Dimethoxy-	Green, soon *brown.*	Pink-purple.	Deep blue-*purple.*	Nil.	
3 : 4 : 6 : 7-Tetramethoxy-	Deep blue-green, soon brown.	Instant green-blue, orange-red.	Pale straw.	Pale green.	Orange-red.
2 : 3 : 6 : 7-Tetramethoxy-	Instant green, red-purple, dull brown.	Deep red-purple.	Nil.	Emerald, intense green at 100°, red with H_2O.	Indigo, purple at 100°, brown.
Morphothebaine	Dirty violet, lighter.	Yellow, reddish.	Steel-blue, grey-blue, tinge violet, yellow-green.	Nil.	Blood-red, red-brown.
Morphothebaine dimethyl ether	Violet, brown.	Pale yellow.	Dull green.	Nil.	Bright brown, duller.
*iso*Thebaine	Olive, brown.	Yellow.	Blue, green, olive, bright green.	Nil.	Dark violet, red-brown, yellow.
*iso*Thebaine methyl ether	Olive-green, dull brown.	Yellow.	Nil, bright green.	Nil.	Dark violet, red-violet, brown.
Apomorphine	Instant green, indigo, dull green.	Dull green, blood-red.	Violet, brown, dull purple.	Pale straw, brown-violet at 100°.	Purple-red, orange-red at 100°.
Boldine	—	Green.	—	Blue (in acetic *acid)*	—

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THE UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

THE DYSON PERRINS LABORATORY, OXFORD.

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XCVI.—*Trypanocidal Activity and Chemical Constitution. Part I. New Sulphur Derivatives of Aromatic Organic Arsenicals.*

By JOHN GARWOOD EVERETT.

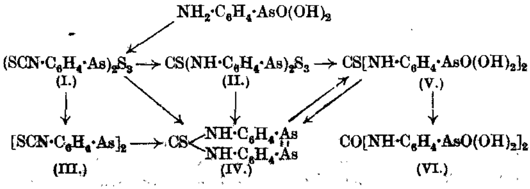
THE observation that neosalvarsan and sulpharsphenamine are more lastingly curative than salvarsan base against experimental infections of *Trypanosoma equiperdum* in mice led to the present research, which was undertaken to determine whether the presence of sulphur in the molecule influences permanency of cure.

Compounds containing the thiocarbonyl group, :C:S, attached to nitrogen were first considered, as these contain an arrangement of nitrogen, carbon, and sulphur atoms similar to that of the side chains of neosalvarsan and sulpharsphenamine, if in these it is assumed that sulphur is attached to carbon, for which view there is some evidence (Newbery and Phillips, J., 1928, 119; Raschig, *Ber.*, 1926, 59, 859; Binz, *ibid.*, p. 1695). Only three compounds

of this type have been previously described, *viz.*, allylthiocarbamyl-*p*-arsanilic acid and its methyl homologue (Thoms, D.R.-P. 294,632) and thiocarbamyl-*p*-arsanilic acid (Morgan, "Organic Compounds of Arsenic and Antimony," p. 162).

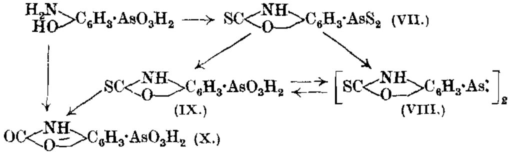
In the present instance, aminophenylarsinic acids were condensed with carbon disulphide in presence of alcohol and sodium hydroxide: the thiocarbonyl group entered the amino-group, and the sulphides formed attacked the arsinic acid group, giving thioarsenates, which on acidification yielded amorphous sulphides. From *p*-arsanilic acid, pp′-*dithiocarbiminophenylarsenic sesquisulphide* (I) was obtained instead of the expected diphenylthiourea-*pp*′-arsenic sesquisulphide (II). The constitution of (I) was shown as follows: On hydrolysis with sodium hydroxide it yielded *diphenylthiourea*-pp′-*arsenic sesquisulphide* (II), and on reduction with sodium hyposulphite pp′-*dithiocarbiminoarsenobenzene* (III), completely soluble in 5% sodium hydroxide solution, was obtained. This on hydrolysis with sodium hydroxide gave pp′-*arseno(diphenylthiourea)* (IV), insoluble in that reagent and identical with the compound obtained by reduction of the sulphide (II), by simultaneous reduction and hydrolysis of the sulphide (I), and by reduction of *diphenylthiourea*-pp′-*diarsinic acid* (V).

pp′-Arseno(diphenylthiourea) (IV) gave, on treatment with iodine, diphenylthiourea-*pp*′-diarsinic acid (V) identical with that obtained either by iodine oxidation of the sulphide (II) or by treatment of *p*-arsanilic acid with thiocarbonyl chloride; and (V) in presence of excess of sodium bicarbonate reacted further with iodine, giving diphenylurea-*pp*′-diarsinic acid (VI), identical with the substance obtained by the action of carbonyl chloride on *p*-arsanilic acid. These reactions are summarised below. The analogy between the arsenated and the non-arsenated compounds was established by boiling phenylthiocarbimide with sodium hydroxide, complete conversion into thiocarbanilide occurring.

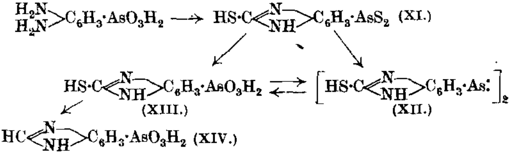


(Formulæ II and IV are so represented for simplicity. The possibility of more extended ring structure is recognised.)

3-Amino-4-hydroxyphenylarsinic acid gave 1-*thiobenzoxazolone*-4-*arsenic disulphide* (VII), which on reduction with sodium hyposulphite gave 4 : 4′-*arseno*-(1-*thiobenzoxazolone*) (VIII). This arseno-compound and the disulphide (VII), on treatment with iodine, both yielded 1-*thiobenzoxazolone*-4-*arsinic acid* (IX) identical with that obtained by treating 3-amino-4-hydroxyphenylarsinic acid with thiocarbonyl chloride. This acid (IX) in presence of excess of sodium bicarbonate reacted further with iodine, giving benzoxazolone-4-arsinic acid (X) identical with the acid obtained by the action of carbonyl chloride on 3-amino-4-hydroxyphenylarsinic acid. These reactions are summarised as follows :



3:4-Diaminophenylarsinic acid gave 2-*thiolbenziminazole*-5-*arsenic disulphide* (XI), and steps similar to the above were taken to prove its constitution : the results are shown below. 2-*Thiolbenziminazole*-5-*arsinic acid* (XIII) on oxidation with iodine in presence of sodium bicarbonate gave *benziminazole*-5-*arsinic acid* (XIV), no trace of 2 : 3-dihydrobenziminazolone-5-arsinic acid being detected.



From the above facts it is clear that, in the compounds mentioned, sulphur attached to arsenic only (sulphide sulphur) may be sharply differentiated from sulphur attached to carbon or carbon and hydrogen only (mercaptan sulphur) by means of either sodium hyposulphite or iodine, the mercaptan sulphur not being oxidised by iodine unless sodium bicarbonate (or some other alkali) is present. Further, the three arsinic acids (V), (IX), and (XIII) gave no colour with an alkaline solution of sodium nitroprusside, whereas all the sulphides mentioned gave a deep violet colour with this reagent.

With a view to a comparison of oxygen with sulphur in analogous compounds, diphenylurea-*pp'*-diarsinic acid (VI), benzoxazolone-4-arsinic acid (X), and 2 : 3-*dihydrobenziminazolone-5-arsinic acid* were prepared and reduced to the corresponding arseno-compounds.

Therapeutic Results.—The above-mentioned thiocarbonyl compounds and their carbonyl analogues have been tested against an experimental infection of *T. equiperdum* in mice with the following results, which amount to a direct comparison of sulphur with oxygen: T = maximum tolerated dose in mg./g. of mouse, c = minimum curative dose in mg./g. of mouse, r = number of days elapsing between cure and reappearance of trypanosomes in the peripheral blood-stream, i = intravenous, and o = oral.

Thiocarbonyl compounds.		*T*.	*c*.	*T*/*c*.	*r*.
pp'-Dithiocarbiminophenylarsenic sesquisulphide (I)	*i*	0·05	0·05	1·0	13
	o	3·0	>3·0	nil	
Diphenylthiourea-*pp'*-arsenic sesquisulphide (II)	*i*	0·01	0·01	1·0	4
	o	2·0	2·0	1·0	12
2-*Thiolbenziminazole-5-arsenic disulphide* (XI)	*i*	0·05	0·006	8·0	>30
	o	10·0	0·2	50·0	14
1-Thiobenzoxazolone-4-arsenic disulphide (VII)	*i*	0·02	0·02	1·0	6
	o	1·0	>1·0	nil	
pp'-Dithiocarbiminoarsenobenzene (III)	*i*	0·025	0·02	1·0	20
	o	2·0	0·7	3·0	7
pp'-Arseno(diphenylthiourea) (IV)	*i*		insoluble		
	o	>10·0	3·0	>3·0	15
5 : 5'-*Arseno-(2-thiolbenziminazole)* (XII)	*i*	0·1	0·005	20·0	>30
	o	>10·0	0·05	>200·0	12
4 : 4'-Arseno-(1-thiobenzoxazolone) (VIII)	*i*	0·07	0·05	1·5	1
	o	4·0	2·0	2·0	10
Diphenylthiourea-*pp'*-diarsinic acid (V)	*i*	0·6	>0·6	nil	
	o	9·0	1·0	9·0	20
2-Thiolbenziminazole-5-arsinic acid (XIII)	*i*	0·5	0·5	1·0	>30
	o	10·0	0·1	100·0	15
1-*Thiobenzoxazolone-4-arsinic acid* (IX)	*i*	1·0	1·0	1·0	10
	o	0·8	0·8	1·0	10
Carbonyl compounds.					
pp'-Arsenodiphenylurea	*i*	insoluble			
	o	>10·0	4·0	>3·0	6
5 : 5'-Arseno-(2 : 3-dihydrobenziminazolone)	*i*	insoluble			
	o	8·0	0·05	170·0	10
4 : 4'-Arsenobenzoxazolone	*i*	0·05	0·025	2·0	1
	o	4·0	3·0	1·3	8
Diphenylurea-*pp'*-diarsinic acid (VI)	*i*	2·0	>2·0	nil	
	o	16·0	2·0	8·0	12
2 : 3-*Dihydrobenziminazolone-5-arsinic acid*	*i*	0·6	0·3	2·0	6
	o	16·0	0·1	160·0	7
Benzoxazolone-4-arsinic acid (X)	*i*	1·0	0·5	2·0	12
	o	1·0	0·1	10·0	10

Conclusions.—(1) From the last column it is seen that permanency of cure is not appreciably influenced by the substitution of sulphur

for oxygen, except in the case of those compounds containing arsenic in the 5-position in a 2-thiolbenziminazole ring, which are outstandingly efficacious.

(2) Considering the results as a whole, it is evident that the substitution of sulphur for oxygen in these compounds causes no appreciable difference in either toxicity or therapeutic activity, and this is of interest since it has already been shown (King and Murch, J., 1925, **127**, 2632; King, Hewitt, and Murch, J., 1926, 1355; Durham, Marchal, and King, *J. Pharm. Exp. Ther.*, 1926, **28**, 341) that the substitution of sulphur for carbon in another series of arsenicals destroys trypanocidal activity *in vivo*, the groups compared in this case being SO_2·NH (sulphonamide) and CO·NH (carbonamide).

EXPERIMENTAL.

[In many cases where the percentages of arsenic, nitrogen, and sulphur found are rather widely divergent from the theoretical values, ordinary criteria of purity are inapplicable owing to the amorphous nature of the compounds. The atomic ratios found for the same compound obtained in different ways are, however, satisfactory. To justify reliance on these values, C, H, S, N, As ratios have been determined in one case, that of 4 : 4′-arseno-(1-thiobenzoxazolone).]

pp′-*Dithiocarbiminophenylarsenic Sesquisulphide* (I).—*p*-Arsanilic acid (22 g.) and carbon disulphide (60 g.) were boiled under reflux with ethyl alcohol (200 c.c.) for 2 hours and cooled, sodium hydroxide solution (25%; 50 c.c.) was added, and boiling continued for 4 hours. Alcohol and carbon disulphide were then removed by distillation and the residue was dissolved in warm water and acidified (Congo-red) with hydrochloric acid. The precipitated *sesquisulphide* was dissolved in boiling sodium carbonate solution (20%), treated with charcoal, again precipitated, and treated with carbon disulphide to remove free sulphur (yield, 18 g.; 70%) (Found: As, 25·0; N, 4·6; S, 26·3; atomic ratios As : N : S = 2·00 : 1·97 : 4·94. $C_{14}H_8N_2S_5As_2$ requires As, 29·2; N, 5·5; S, 31·1%). It was obtained as a light yellow, amorphous solid insoluble in water, acids, or organic solvents, but soluble in excess of cold sodium hydroxide solution or in excess of boiling sodium carbonate solution.

The two following disulphides were prepared similarly and had similar physical properties: 1-*Thiobenzoxazolone-4-arsenic disulphide* (VII), from 3-amino-4-hydroxyphenylarsinic acid (yield, 64%) (Found: As, 22·0; N, 4·0; S, 28·2; atomic ratios As : N : S = 1·00 : 0·97 : 3·02. $C_7H_4ONS_3As$ requires As, 25·9; N, 4·8; S, 33·2%), is soluble in dilute solutions of sodium cyanide: this is a

characteristic property of 1-thiobenzoxazolone. *2-Thiolbenziminazole-5-arsenic disulphide* (XI), from 3 : 4-diaminophenylarsinic acid (yield, 64%) (Found: As, 20·8; N, 7·8; S, 26·9; atomic ratios As : N : S = 1·00 : 2·00 : 3·03. $C_7H_5N_2S_3As$ requires As, 26·0; N, 9·7; S, 33·3%).

Diphenylthiourea-pp'-*arsenic sesquisulphide* (II) was obtained, by boiling *pp'*-dithiocarbiminophenylarsenic sesquisulphide (10 g.) for 6 hours with sodium hydroxide solution (25%, 50 c.c.), and acidifying the cooled solution (Congo-red) with hydrochloric acid, as a light yellow, amorphous solid resembling (I) in solubility (Found: As, 28·4; N, 5·2; S, 24·5; atomic ratios As : N : S = 1·00 : 0·98 : 2·02. $C_{13}H_{10}N_2S_4As_2$ requires As, 31·8; N, 5·9; S, 27·1%).

pp'-*Dithiocarbiminoarsenobenzene* (III).—*pp'*-Dithiocarbiminophenylarsenic sesquisulphide (30 g.) was mixed with water (300 c.c.) and just sufficient sodium hydroxide to effect solution. Sodium hyposulphite (375 g.) and sodium hydroxide (7·5 g.) were dissolved in water (3 l.). The two solutions were mixed and kept at 55° for 1 hour. The precipitated *arseno-compound*, after being washed with water and dried in a vacuum over concentrated sulphuric acid, was obtained as a light yellow, amorphous solid, soluble in 5% sodium hydroxide solution (yield, 18 g.; 74%) (Found: As, 33·7; N, 6·2; S, 14·35; atomic ratios As : N : S = 1·00 : 0·99 : 0·99. $C_{14}H_8N_2S_2As_2$ requires As, 35·9; N, 6·7; S, 15·3%).

(Unless otherwise stated, reduction with sodium hyposulphite was carried out as above.)

pp'-*Arseno(diphenylthiourea)* (IV).—(1) *pp'*-Dithiocarbiminophenylarsenic sesquisulphide was reduced with sodium hyposulphite as described above, except that sodium hydroxide solution (25%; 100 c.c.) was added, and the temperature kept at 90° (yield, 40%) (Found: As, 34·4; N, 6·2; S, 8·0; atomic ratios As : N : S = 2·00 : 1·92 : 1·08. $C_{13}H_{10}N_2SAs_2$ requires As, 39·9; N, 7·4; S, 8·5%).

(2) Diphenylthiourea-*pp'*-arsenic sesquisulphide was reduced with sodium hyposulphite (yield, 62%) (Found: As, 35·0; N, 6·4; S, 8·1%; atomic ratios As : N : S = 2·00 : 1·96 : 1·08).

(3) Diphenylthiourea-*pp'*-diarsinic acid was reduced with sodium hyposulphite (yield, 71%) (Found: As, 36·3; N, 6·7; S, 7·9%; atomic ratios As : N : S = 2·00 : 1·98 : 1·02).

(4) A solution of *pp'*-dithiocarbiminoarsenobenzene (4 g.) in sodium hydroxide solution (20%; 100 c.c.) was boiled for 15 minutes and the precipitate was removed, washed with water, and dried in a vacuum over sulphuric acid (yield, 3 g.; 81%) (Found: As, 36·5; N, 6·8; S, 7·8%; atomic ratios As : N : S = 2·00 : 1·98 : 1·00).

pp'-*Arseno(diphenylthiourea)* was obtained by these four methods as an orange, amorphous solid insoluble in sodium hydroxide.

4 : 4'-*Arseno-(1-thiobenzoxazolone)* (VIII).—(1) 1-Thiobenzoxazolone-4-arsenic disulphide was reduced with sodium hyposulphite (yield, 73%) (Found: C, 33·6, 33·2; H, 2·5, 2·3; N, 5·7, 5·8; S, 13·4, 13·6; As, 31·0, 31·3; atomic ratios C : H : N : S : As = 6·8 : 5·7 : 0·99 : 1·02 : 1·00. $C_{14}H_8O_2N_2S_2As_2$ requires C, 37·4; H, 1·8; N, 6·2; S, 14·2; As, 33·3%). The loss in a vacuum over sulphuric acid was 1·8% and ash 3%.

(2) 1-Thiobenzoxazolone-4-arsinic acid was reduced with sodium hyposulphite (yield, 70%) (Found: As, 32·0; N, 6·1; S, 13·9%; atomic ratios As : N : S = 1·00 : 1·02 : 1·02).

4 : 4'-*Arseno-(1-thiobenzoxazolone)* obtained by these two methods was a light yellow, amorphous powder, soluble in sodium hydroxide solution and very readily soluble in dilute solutions of sodium cyanide.

5 : 5'-*Arseno-(2-thiolbenziminazole)* (XII).—(1) 2-Thiolbenziminazole-5-arsenic disulphide was reduced with sodium hyposulphite (yield, 72%) (Found: As, 30·0; N, 11·2; S, 12·9; atomic ratios As : N : S = 1·00 : 2·01 : 1·01. $C_{14}H_{10}N_4S_2As_2$ requires As, 33·5; N, 12·5; S, 14·3%).

(2) Thiolbenziminazole-5-arsinic acid was reduced with sodium hyposulphite (yield, 68%) (Found: As, 30·7; N, 11·5; S, 13·1%; atomic ratios As : N : S = 1·00 : 2·01 : 1·01).

5 : 5'-*Arseno-(2-thiolbenziminazole)* obtained by these two methods was a light yellow, amorphous powder, readily soluble in dilute solutions of sodium hydroxide.

pp'-*Arseno(diphenylurea)* was obtained as an orange amorphous powder, insoluble in sodium hydroxide solution, by reduction of diphenylurea-*pp'*-diarsinic acid with sodium hyposulphite (yield 80%) (Found: As, 36·0; N, 6·6; atomic ratio As : N = 1·00 : 0·9[illegible] $C_{13}H_{10}ON_2As_2$ requires As, 41·6; N, 7·8%).

4 : 4'-Arsenobenzoxazolone was prepared by Fargher's method (J 1919, **115**, 991) and obtained as a light yellow, amorphous powde[r] soluble in sodium hydroxide solution (Found: As, 31·5; N, 5·[illegible] atomic ratio As : N = 1·00 : 1·00. Calc.: As, 35·7; N, 6·7%).

5 : 5'-*Arseno-(2 : 3-dihydrobenziminazolone)* was obtained as yellow, amorphous powder, insoluble in sodium hydroxide solutio[n] by reduction of 2 : 3-dihydrobenziminazolone-5-arsinic acid wi[th] sodium hyposulphite (yield, 85%) (Found: As, 33·2; N, 12·[illegible] atomic ratio As : N = 1·00 : 2·01. $C_{14}H_{10}O_2N_4As_2$ requires A[s] 36·1; N, 13·5%).

Diphenylthiourea-pp'-*diarsinic Acid* (V).—(1) Thiocarbon[yl] chloride (6 g.) was added gradually with vigorous shaking

p-arsanilic acid (22 g.) dissolved in *N*-sodium hydroxide (180 c.c.), alkalinity being maintained by the addition of sodium hydroxide solution (20%) as required. The filtered solution, after treatment with charcoal, was acidified (Congo-red) with hydrochloric acid and the diarsinic acid obtained was dissolved in sodium bicarbonate solution, reprecipitated, and finally recrystallised from 50% alcohol (yield, 17 g.; 69%) (Found on acid dried at 80°: As, 31·5; N, 5·8; S, 6·8. $C_{13}H_{14}O_6N_2SAs_2$ requires As, 31·5; N, 5·9; S, 6·7%).

(2) *pp'*-Arseno(diphenylthiourea) (3·8 g.) was stirred with water (20 c.c.), and *N*/10-iodine added gradually until no more was absorbed (500 c.c.). A solution of the precipitate in aqueous sodium bicarbonate (6%; 60 c.c.) was treated with charcoal, filtered, and acidified (Congo-red) with hydrochloric acid (yield, 2 g.; 42%) (Found on acid dried at 80°: As, 31·4; N, 5·8; S, 6·7%).

(3) Diphenylthiourea-*pp'*-arsenic sesquisulphide (4·7 g.) was stirred with water (20 c.c.), and *N*/10-iodine added (300 c.c.). The precipitate was treated as described under (2) (yield, 1·5 g.; 31%) (Found on acid dried at 80°: As, 31·4; N, 5·7; S, 6·8%).

*Diphenylthiourea-*pp'*-diarsinic acid* was thus obtained in rosettes of fine pale yellow needles. It is insoluble in cold water or dilute mineral acids, sparingly soluble in hot water, and moderately easily soluble in warm alcohol. The calcium and magnesium salts are amorphous and the barium salt is micro-crystalline.

2-*Thiolbenziminazole*-5-*arsinic acid* (XIII) was obtained (1) from 3 : 4-diaminophenylarsinic acid (23 g.) and thiocarbonyl chloride (12 g.) as described under diphenylthiourea-*pp'*-diarsinic acid, excluding the final recrystallisation from alcohol (yield, 21 g.; 78%) (Found on acid dried at 80°: As, 27·3; N, 10·2; S, 11·8. $C_7H_7O_3N_2SAs$ requires As, 27·4; N, 10·2; S, 11·7%), (2) from 5 : 5'-arseno-(2-thiolbenziminazole) (4·5 g.) and *N*/10-iodine (500 c.c.) as described under diphenylthiourea-*pp'*-diarsinic acid (yield, 2 g.; 36%) (Found on acid dried at 80°: As, 27·3; N, 10·1; S, 11·6%), and (3) from 2-thiolbenziminazole-5-arsenic disulphide (2·9 g.) and *N*/10-iodine (200 c.c.) as described under diphenylthiourea-*pp'*-diarsinic acid (yield, 1 g.; 37%) (Found on acid dried at 80°: As, 27·3; N, 10·1; S, 11·8%).

The arsinic acid was obtained by these three methods in small buff needles, insoluble in cold water or dilute mineral acids, moderately easily soluble in hot water, and readily soluble in warm alcohol. The calcium salt forms rosettes of needles, and the barium salt fine needles; the magnesium salt is amorphous.

1-*Thiobenzoxazolone*-4-*arsinic acid* (IX) was obtained (1) from 3-amino-4-hydroxyphenylarsinic acid as described under 2-thiolbenziminazole-5-arsinic acid (yield, 78%) (Found on acid dried at 80°:

As, 27·3; N, 5·1; S, 11·7. $C_7H_6O_4NSAs$ requires As, 27·3; N, 5·1; S, 11·6%), (2) from 4 : 4′-arseno-(1-*thiobenzoxazolone*) as described under 2-thiolbenziminazole-5-arsinic acid (yield, 45%) (Found on acid dried at 80°: As, 27·2; N, 5·1; S, 11·7%), and (3) from 1-thiobenzoxazolone-4-arsenic disulphide as described under 2-thiolbenziminazole-5-arsinic acid (yield, 30%) (Found on acid dried at 80°: As, 27·2; N, 5·0; S, 11·8%). It formed small, pale yellow needles, insoluble in cold water or dilute mineral acids, sparingly soluble in hot water, and moderately easily soluble in warm alcohol. The magnesium salt is amorphous.

Diphenylurea-pp′-*diarsinic Acid* (VI).—This was obtained (1) from *p*-arsanilic acid and carbonyl chloride, essentially as described in D.R.-P. 191548 (Found on acid dried at 80°: As, 32·5; N, 6·0. Calc.: As, 32·6; N, 6·1%), and (2) from diphenylthiourea-*pp*′-diarsinic acid (2·4 g.), dissolved in water (60 c.c.) and sodium bicarbonate (20 g.), and *N*/2-iodine (40 c.c.). The colourless solution, after treatment with charcoal, was filtered and acidified (Congo-red) with hydrochloric acid; the precipitated acid was dissolved in sodium bicarbonate solution and reprecipitated (yield, 1 g.; 43%) (Found on acid dried at 80°: As, 32·7; N, 6·1%).

Diphenylurea-*pp*′-diarsinic acid forms small white needles, insoluble in cold water or dilute mineral acids, sparingly soluble in hot water or alcohol. The calcium and magnesium salts are amorphous; the barium salt forms rosettes of small prisms.

Benzoxazolone-4-arsinic acid (X), obtained (1) by Fargher's method (*loc. cit.*) (Found on acid dried at 80°: As, 28·9; N, 5·4. Calc.: As, 29·0; N, 5·4%) and (2) from 1-thiobenzoxazolone-4-arsinic acid (2·75 g.) and *N*/2-iodine (80 c.c.) as described under diphenylurea-*pp*′-diarsinic acid (yield, 2 g.; 77%) (Found on acid dried at 80°: As, 28·6; N, 5·2%), formed prismatic needles, insoluble in cold water or dilute mineral acids and readily soluble in hot water or alcohol.

2 : 3-Dihydrobenziminazolone-5-arsinic acid, obtained from 3 : 4-diaminophenylarsinic acid and carbonyl chloride essentially as described by Bertheim (*Ber.*, 1911, **44**, 3097) (Found on acid dried at 80°: As, 29·0; N, 10·7. Calc.: As, 29·1; N, 10·8%), formed small prisms, insoluble in cold water or dilute mineral acids and sparingly soluble in hot water or alcohol. The calcium salt crystallised in feathery needles, the magnesium salt in rosettes of fine needles, and the barium salt in large plates.

Benziminazole-5-arsinic acid (XX), obtained from 2-thiolbenziminazole-5-arsinic acid (1·4 g.) and *N*/2-iodine (40 c.c.) as described under diphenylurea-*pp*′-diarsinic acid (yield, 1 g.; 83%) (Found on acid dried at 80°: As, 31·0; N, 11·6. Calc.: As, 31·0; N,

11·5%), formed rosettes of needles, insoluble in cold water, sparingly soluble in hot water or alcohol, and readily soluble in dilute mineral acids. The magnesium salt is amorphous and the barium and calcium salts are microcrystalline (compare Baxter and Fargher, J., 1919, **115**, 1372; Phillips, J., 1928, 3137).

Conversion of Phenylthiocarbimide into Thiocarbanilide.—The thiocarbimide (10 g.) was boiled under reflux for 1 hour with sodium hydroxide solution (20%; 100 c.c.). The resulting thiocarbanilide was removed, washed with water, and recrystallised from hot alcohol (yield, 8·0 g.; 94%). M. p. 153° (alone or mixed with an authentic specimen).

Messrs. May & Baker, Ltd.,
Wandsworth, S.W. 18. [*Received, January 10th, 1929.*]

XCVII.—*The Densities of Butyric Acid–Water Mixtures.*

By John Grindley and Charles R. Bury.

In a previous communication from this laboratory (Jones and Bury, *Phil. Mag.*, 1927, **4**, 841), it was suggested that aqueous solutions of butyric acid contain micelles resembling those that exist in soap solutions (McBain and Salmon, *J. Amer. Chem. Soc.*, 1920, **42**, 426). This conclusion was based on a study of freezing points; in particular, the " A plot," used in the graphical evaluation of activities (Lewis and Randall, " Thermodynamics," 1923, p. 287), is related to that of the lower fatty acids in exactly the same manner as the " A plots " of the soaps are related to those of the sodium salts of the lower fatty acids (Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517). Further, the hypothesis is not improbable from a structural point of view: butyric acid belongs to that class of substances the molecules of which consist of a hydrocarbon chain combined with a polar group and tend to form unimolecular layers on the surface of water and micelles in water, when they are soluble in it. Since the soaps are strong electrolytes, the formation of micelles—or aggregates of anions—must involve considerable work against the electrical forces; it would therefore be expected that weaker electrolytes should form micelles more readily. Butyric acid is a weak electrolyte, so it is not improbable that it should form micelles even though its hydrocarbon chain contains far fewer carbon atoms than are present in typical colloidal soaps.

In order to test the above suggestion, we have relied on the following considerations. Micelle formation can be regarded thermo-

dynamically as an extreme case of association (complicated, in the case of soaps, by ionisation; with butyric acid, however, ionisation can be neglected except in very dilute solutions, with which this work is not concerned). Micelle formation can be represented by the equation $nC_3H_7{\cdot}CO_2H \rightleftharpoons (C_3H_7{\cdot}CO_2H)_n$, where n is the number of simple molecules in a micelle. If s and m are the concentrations of butyric acid as simple molecules and as micelles, respectively, and if the equilibrium constant be written in the form K^n (K being the Haber form of the constant), then, assuming as a first approximation that the activity coefficients of the two molecular species are unity, we have $s^n/m = K^n$ or $(s/K)^n = m$. Since n is a relatively large number, it follows that, if s/K is appreciably smaller than unity, m will be negligibly small, *i.e.*, the concentration of micelles will be negligible until the total concentration approaches the value K. In the neighbourhood of this point the concentration of micelles will first become appreciable, and will rapidly increase as the total concentration increases. Consequently, if any physical property of aqueous butyric acid solutions be plotted against the concentration, the slope of the curve will change abruptly * near this point: in other words, partial molal (or specific) quantities will change abruptly when the concentration has the value K. From freezing-point data, this concentration should be approximately 15% of acid.

None of the physical properties of butyric acid–water mixtures has been measured with sufficient thoroughness to test this conclusion, and we have therefore determined their densities and thence calculated the partial specific volumes of the two constituents. In order to find the effect of temperature on the concentration at which the slope changes abruptly, determinations have been made at five temperatures.

EXPERIMENTAL.

The procedure recommended by Hartley and Barrett (J., 1911, **99**, 1072) for the determination of densities was followed, with two exceptions. First, their formula requires modification when applied to a liquid of which the temperature coefficient of expansion is much greater than that of water (Grindley, J., 1928, 3297); and secondly, a small flask with restricted neck, of the type used by Baxter and Wallace (*J. Amer. Chem. Soc.*, 1916, **38**, 70), was used.

* Some observers have claimed that the slopes of certain property–composition curves change discontinuously at certain points (*e.g.*, Mendeléeff, "Principles of Chemistry," 1891, vol. 2, p. 237). With micelle formation, the greater the value of n, the more abrupt the change of slope will be, but only in the limiting case, when n is infinite, could it become discontinuous.

This was found more convenient than the pyknometers of Hartley and Barrett when carrying out a series of determinations on the same liquid at temperatures extending from 0° to 35°. The flask was blown from a test-tube and had a capacity of about 28 c.c.: a counterpoise of similar form, and made from the same glass, was used. The weight of the flask, when filled with water at any given temperature and weighed against the counterpoise, was reproducible to ± 0·1 mg. Weights were standardised by the method of Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

As starting point for the preparation of pure butyric acid, British Drug Houses' "normal butyric acid" (freezing point − 10°) and Kahlbaum's "normal (purest) butyric acid" (freezing point − 12°) were used: no other samples examined could be made to freeze above − 21°. By fractionally freezing ten times, care being taken to avoid the introduction of moisture, the freezing point was raised to − 7·1°. The purified acid apparently still contained traces of water, for, after shaking with phosphoric oxide in the cold, the freezing point was raised to − 6·70° ± 0·05° (mean of determinations with two independently purified samples): when about half the material was frozen the freezing point was 0·15° lower, from which it is probable that the freezing point of the pure acid is about − 6·55°.* The freezing points were determined by the Beckmann method with a standardised thermometer, graduated to 0·1°.

Unfortunately, the phosphoric oxide cannot be satisfactorily separated from the acid; distillation, even at low pressures, gives rise to the anhydride and to some sweet-smelling impurity. The phosphoric oxide adheres to the walls of the vessel, and most of it is removed by decantation through a filter; the acid so obtained, however, was found by analysis to contain 0·04% P_2O_5, but was used for density determinations of the pure acid only. In preparing the butyric acid–water mixtures, the acid, purified by crystallisation and then distilled in a vacuum, was mixed with a suitable amount of conductivity water, the final concentration being determined by titration with baryta.

The most important sources of error in this work appear to be the analytical error in determining the concentrations of the acid (about 0·1%), and the uncertainty as to the exact temperatures of

* Previous determinations of the freezing point of butyric acid are − 2° to + 2° (Linnemann, *Annalen*, 1871, **160**, 228); − 3·12° (Faucon, *Compt. rend.*, 1909, **148**, 1189); − 4·5° to − 2·0° (Zander, *Annalen*, 1884, **224**, 63); − 4·5° (Baflo, *Z. physikal. Chem.*, 1910, **72**, 448); − 4·65° to − 4·70° (English and Turner, *J.*, 1915, **107**, 779); and − 7·9° (Schneider, *Z. physikal. Chem.*, 1897, **22**, 223).

the thermostats. These could be regulated to within 0·02° of the desired temperature, an uncertainty which might lead to an error of 2×10^{-5} in the density of the most expansible (*i.e.*, concentrated) solutions.

TABLE I.

Acid, %.	$D^{0°}_{4°}$.	$D^{12°}_{4°}$.	$D^{18°}_{4°}$.	$D^{25°}_{4°}$.	$D^{34·94°}_{4°}$.
0	0·99987	0·99953	0·99862	0·99707	0·99408
4·905	1·00379	1·00250	1·00122	0·99930	0·99577
7·505	1·00587	1·00408	1·00256	1·00038	0·99657
10·01	1·00785	1·00546	1·00371	1·00127	0·99713
11·74	1·00912	1·00631	1·00436	1·00173	0·99736
13·94	1·01045	1·00707	1·00491	1·00207	0·99745
15·59	1·01124	1·00746	1·00517	1·00214	0·99738
17·39	1·01177	1·00766	1·00522	1·00207	0·99714
19·21	1·01218	1·00777	1·00521	1·00196	0·99688
20·86	1·01240	1·00781	1·00516	1·00179	0·99657
23·85	1·01264	1·00769	1·00489	1·00135	0·99594
26·93	1·01274	1·00748	1·00453	1·00082	0·99520
30·07	1·01277	1·00719	1·00409	1·00021	0·99435
35·05	1·01270	1·00662	1·00327	0·99913	0·99294
40·06	1·01251	1·00591	1·00233	0·99792	0·99138
45·31	1·01221	1·00502	1·00120	0·99651	0·98959
50·13	1·01177	1·00406	0·99996	0·99506	0·98781
54·09	1·01130	1·00314	0·99887	0·99374	0·98622
58·08	1·01066	1·00210	0·99767	0·99234	0·98453
60·23	1·01026	1·00145	0·99692	0·99147	0·98356
61·93	1·00986	1·00090	0·99629	0·99078	0·98272
63·32	1·00954	1·00045	0·99578	0·99016	0·98206
66·00	1·00880	0·99949	0·99465	0·98898	0·98070
70·02	1·00747	0·99774	0·99280	0·98695	0·97845
74·07	1·00573	0·99566	0·99057	0·98452	0·97580
77·90	1·00372	0·99336	0·98812	0·98194	0·97306
81·56	1·00140	0·99080	0·98546	0·97917	0·97010
85·96	0·99801	0·98711	0·98163	0·97521	0·96598
90·95	0·99310	0·98191	0·97626	0·96968	0·96030
95·62	0·98715	0·97561	0·96983	0·96312	0·95351
100	0·97844	0·96642	0·96045	0·95350	0·94367

The results are given in Table I; in the first column is given the concentration of acid in g. per 100 g. of solution, and in the remaining columns are given the densities ($D^{t°}_{4°}$) at 0°, 12°, 18°, 25°, and 34·94°. The density of pure butyric acid, over the range studied, is given by the formula

$$D^{t°}_{4°} = 0·97844 - 0·001004t + 2·5 \times 10^{-7}t^2.$$

Values calculated from this formula are in good agreement with the determinations of Brühl (*Annalen*, 1880, **203**, 80) and Eijkman (*Rec. trav. chim.*, 1893, **12**, 157). The densities of solutions shown in the table are in fair agreement with measurements at 25° and 35° by Drucker (*Z. physikal. Chem.*, 1905, **52**, 649), whose work refers mainly to dilute solution, and at 25° by Ludeking (*Ann. Physik*, 1886, **27**, 72), whose results cover the whole range of concentrations but are not accurate enough for the purpose in view.

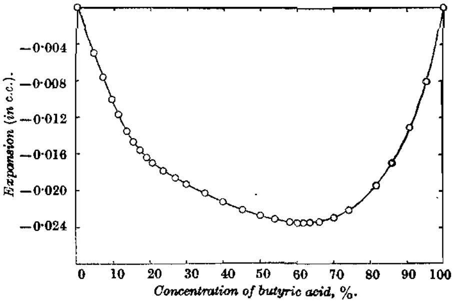
The change of density with concentration is unsuitable for

illustration in a small-scale graph; we have therefore plotted in Fig. 1 the expansion on formation of 1 g. of solution from its constituents (ΔV) at 0° against the percentage composition of the solution. If d is the density of a solution containing $x\%$ of acid, and d' and d'' are the densities of the pure acid and water respectively at the same temperature,

$$\begin{aligned}\Delta V &= 1/d - x/100d' - (100 - x)/100d'' \\ &= 1/d - 1/d'' + x(1/d'' - 1/d')/100,\end{aligned}$$

the second form of the equation being more suitable for numerical calculations. An abrupt change in the slope of the curve, such as

FIG. 1.

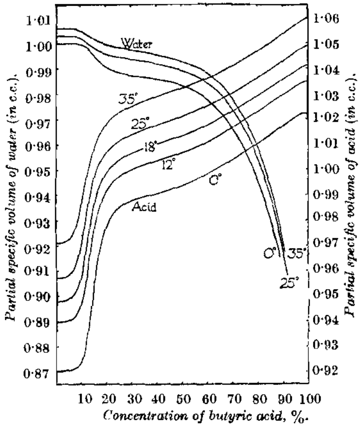


we had been led to expect, is noticeable at a concentration of about 15% of acid. At higher temperatures the curves obtained are of the same general form.

Partial specific volumes of water and acid have been evaluated by a graphical method described by Hildebrand ("Solubility," American Chemical Society Monograph, 1924, p. 64) and are shown in Fig. 2 (for the sake of clearness the values for water at 12° and 18° are omitted). The partial specific volume of water changes very rapidly when its concentration is low, and it is impossible to calculate its limiting value (in pure acid) from our data. The limiting value given for the partial specific volume of butyric acid in pure water is also doubtful, since we have not made a special study of extremely dilute solutions, where the effect of ionisation would become appreciable. Fig. 2 shows that the partial specific volumes of both constituents change very rapidly when the con-

centration is about 12—15% of acid; that, as the temperature is raised, the change tends to become less abrupt; and that the concentration at which the change is greatest decreases with rise of temperature, being 15·0% of acid at 0°, 13·7% at 12°, 13·0% at 18°, 12·3% at 25°, and 12·0% at 35°. The results of this work confirm, therefore, the existence of micelles in butyric acid solutions.

FIG. 2.



Summary.

It is argued that micelle formation must lead to abrupt changes in the slope of physical property–composition curves.

The densities of butyric acid–water mixtures at 0°, 12°, 18°, 25°, and 35° have been measured and partial specific volumes calculated.

The results obtained support the contention of Jones and Bury that micelle formation occurs in these solutions.

EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH. [*Received, November 6th, 1928.*]

XCVIII.—*Chromatocobaltiammines. Part II. The Dichromatotetramminecobaltiates and the Maximum Co-ordination Number of Cobalt.*

By Samuel Henry Clifford Briggs.

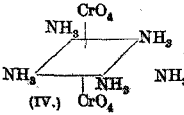
In a former paper (J., 1919, **115**, 67) it was shown that the chromate radical may constitute part of a complex kation, filling either one co-ordination position, as in the chromatopentamminecobaltic salts (I), or two positions, as in the chromatotetramminecobaltic series (II). In the present paper a series of compounds is described in which the chromate radical forms part of a complex anion.

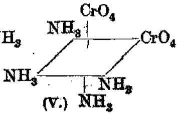
$$\left[Co\begin{matrix}5NH_3\\CrO_4\end{matrix}\right]X \quad \text{(I.)} \qquad \left[Co\begin{matrix}4NH_3\\CrO_4\end{matrix}\right]X \quad \text{(II.)} \qquad M^I\left[Co\begin{matrix}2CrO_4\\4NH_3\end{matrix}\right] \quad \text{(III.)}$$

These compounds, the dichromatotetramminecobaltiates (III), are obtained when a solution of a diaquotetramminecobaltic salt is added to a sufficiently large excess of a concentrated solution of an alkali chromate and the solution is kept for several days at the ordinary temperature. Two crystalline forms have been prepared, one being yellowish-green to deep green and the other greenish-yellow to brown. The presence of dichromate in the solution appears to favour the production of the brown form.

The investigation of these substances is complicated by the fact that they are all decomposed by acids, alkalis, or hot water, and are also only slightly soluble in water and therefore cannot be recrystallised. Their solutions in cold water decompose within a few hours.

If it be assumed that the cobalt atom has the co-ordination number six, then each chromate radical will occupy one co-ordination position, the two radicals having the *trans*-configuration in the green form (IV) and the *cis*-configuration in the brown form (V) as indicated by the colour of the compounds. *Sodium, potassium, lithium*, and *magnesium* salts have been investigated. The sodium and magnesium compounds have been prepared in both forms, whereas only the brown lithium salt and the green potassium salt have been obtained.


(IV.)


(V.)

$$(Mg,6H_2O)\left[Co\begin{matrix}2CrO_4\\4NH_3\\2H_2O\end{matrix}\right]_2 \quad \text{(VI.)}$$

The green magnesium salt appears to have a different constitution

from the others. This salt contains ten molecules of water; six of these, being given off in a few days in a vacuum over sulphuric acid, are presumably the six molecules of water of crystallisation frequently associated with magnesium salts and attached to the magnesium ion, and the other four are evolved very slowly during several weeks, the colour meanwhile changing from green to brown. This colour change shows that the four molecules are associated with the anions. Since the green colour cannot be restored by hydration, the colour change to brown must represent a change in the configuration of the anion itself. Such a change could hardly occur if the water molecules were merely addenda to the anions, and it would therefore appear that they are part of the complex itself, the formula of the compound being (VI), in which the cobalt atom has the co-ordination number eight. From the green colour it may be assumed that the ammonia molecules in (VI) are all in one plane as in (IV), perhaps the diagonal plane of a cube, and on removal of the four water molecules their relative positions are changed, giving the *cis*-form with co-ordination number six (V). On the other hand, if the co-ordination number were eight in all the other compounds of the series, with each chromate radical occupying two co-ordination positions as in (II), and each co-ordination position representing the corner of a cube (compare Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, 1925, **45**, No. 8), then the dichromatotetramminecobaltiates should exist in three forms. It was thought that a third and more soluble form might possibly be present in the very dark solution from which the compounds are prepared, but attempts to isolate it by increasing the proportion of cobalt salt gave only an insoluble *compound* of the formula $Co_2(CrO_4)_3,8NH_3,H_2O$. It should be noted that according to Matsuno (*loc. cit.*) cobalt has the co-ordination number eight in some of the pentammine salts, as shown by the preparation of the compound $[Co(5NH_3)(C_2O_4)Cl]$ in two optically active forms.

It was shown by Rây and Sarkar (*J. Indian Chem. Soc.*, 1925, **1**, 289) that the dichromate radical also may form part of a cobaltiammine co-ordination complex, and this has been confirmed by the preparation of a *compound* of the formula $Co_2(Cr_2O_7)_3,9NH_3,4H_2O$ by the action of an excess of sodium dichromate on diaquotetramminecobaltic nitrate. One molecule of water appears to be constitutional, and the simplest structure is

$$\left[\begin{matrix}4NH_3\\H_2O\end{matrix}Co\cdot Cr_2O_7\cdot Co,5NH_3\right](Cr_2O_7)_2,3H_2O,$$

but as the compound is almost insoluble in water this cannot be definitely decided.

Attempts to prepare ammonium dichromatotetramminecobaltiate

were not successful, a pentammine derivative being obtained. The analysis of this *substance* corresponds to the formula

$$(NH_4)_2CrO_4,\left[Co_{CrO_4}^{5NH_3}\right]_2CrO_4,$$

with co-ordination number six, or $NH_4\left[Co_{2CrO_4}^{5NH_3}\right]$, with co-ordination number eight, but here again the precise determination of the constitution is prevented by the insolubility of the compound.

EXPERIMENTAL.

The general method for preparing the diaquotetramminecobaltic solution was to decompose carbonatotetramminecobaltic nitrate (1 g.) with dilute hydrochloric acid (1 c.c. of concentrated acid to 4 c.c. of water).

Sodium trans-*Dichromatotetramminecobaltiate.*—The solution of the diaquo-compound from 6 g. of carbonatotetramminecobaltic nitrate was added with vigorous stirring in the cold to a solution of 150 g. of sodium chromate tetrahydrate and 5 g. of sodium dichromate dihydrate in 120 c.c. of water, the dichromate being added to reduce the alkalinity of the solution. A green, microcrystalline precipitate began to separate slowly after a few hours, 6·5 g. being deposited during 3 weeks. On adding a solution of diaquotetramminecobaltic salt to the mother-liquor, a further quantity was obtained. The green *compound* was anhydrous (Found : Na, 5·2; Co, 15·4; CrO_3, 52·2; NH_3, 17·8. $Na\left[Co_{4NH_3}^{2CrO_4}\right]$ requires Na, 6·0; Co, 15·4; CrO_3, 52·3; NH_3, 17·8%).

When the salt was shaken with a large amount of cold water it dissolved, leaving a small quantity of a green residue. As it was thought that this might be an impurity with a lower sodium content, 10 g. of the preparation were repeatedly extracted with 750 c.c. of cold water until only 1 g. of solid remained [Found : Na, 4·6; Co, 17·4; CrO_3, 46·7; NH_3, 16·6; H_2O, loss over sulphuric acid, 1·8. $Na_2Co_3(CrO_4)_5OH,10NH_3,2H_2O$ requires Na, 4·5; Co, 17·3; CrO_3, 48·7; NH_3, 16·6; $1H_2O$, 1·8%]. If the material was a homogeneous compound originally present as an impurity, it was evidently a highly complex polynuclear substance. It may, however, have been contaminated by the products of decomposition of the bulk substance by water, and thus it is not possible to draw any definite conclusions as to its constitution.

Sodium *trans*-dichromatotetramminecobaltiate dissolves in about 300 parts of water at 20°. On standing for a few hours in the cold the solution changes in colour from green to yellow and a brown precipitate of impure chromatohydroxotriamminecobalt (J., 1919, **115**, 75) is formed.

Sodium cis-*Dichromatotetramminecobaltiate*.—The solution of diaquotetramminecobaltic salt from 6 g. of the carbonatotetramminecobaltic nitrate was added in the cold to a solution of 110 g. of sodium chromate and 60 g. of hydrated dichromate in 160 c.c. of water. At the winter temperature a mixture of compounds first separated and two fractions were discarded, but the third was homogeneous, consisting of greenish-brown crystals (Found: H_2O, 5·0. A *monohydrate* requires H_2O, 4·5%. Found in anhydrous *compound*: Na, 5·2; Co, 15·4; CrO_3, 52·6; NH_3, 18·0%). The salt was very slightly soluble in water, giving a yellow solution.

Lithium cis-*Dichromatotetramminecobaltiate*.—Lithium chromate was prepared by heating an excess of lithium carbonate with chromic acid on the water-bath and evaporating it to crystallisation, but analysis showed the salt to contain some dichromate. To a solution of this preparation containing 47 g. of the chromate and 9 g. of the dichromate in 100 c.c. of water, a solution of the diaquotetramminecobaltic salt from 4 g. of carbonatotetramminecobaltic nitrate was added; after twelve days, 1·5 g. of greenish-brown crystals had separated (Found: Li, 1·4; Co, 15·1; CrO_3, 50·2 H_2O, 6·6; NH_3, 17·7. $2Li\left[Co{}^{2CrO_4}_{4NH_3}\right],3H_2O$ *requires* Li, 1·8; Co 15·0; CrO_3, 50·9; H_2O, 6·9; NH_3, 17·3%).

Lithium chromate free from dichromate was then prepared b adding to a solution of the mixed chromate and dichromate th calculated amount of a solution of lithium carbonate. The sa obtained by crystallising this solution was used in an attempt t prepare the green lithium compound, but the product was identic with the greenish-brown salt just described.

Potassium trans-*dichromatotetramminecobaltiate* was prepared a very impure condition as a dark green powder when a soluti of the diaquotetrammine nitrate was added to a large excess of concentrated solution of potassium chromate. When a lit dichromate was also present, what appeared to be a mixture of t green and brown forms was produced, but, owing to the sli solubility of potassium dichromate in a solution of chromate, suitable conditions for preparing the brown compound could not attained. The green form was obtained in a purer state accidenta when the mother-liquor from the preparation of trichrom octamminedicobalt (J., 1919, **115**, 73) was kept for some days the neighbourhood of 0°. The compound was analysed after be kept for some months in a desiccator over calcium chloride (Fou K, 8·7; Co, 14·6; CrO_3, 50·5. $K\left[Co{}^{2CrO_4}_{4NH_3}\right]$ requires K, 9·8; ... 50·2%). Its green solution gave a greenish-br

precipitate with copper sulphate, no precipitate with zinc sulphate, and with silver nitrate a brown precipitate which rapidly became dark red, the colour of silver chromate.

Magnesium Salts.—The green compound was prepared by adding the diaquotetramminecobaltic solution from 10 g. of carbonatotetramminecobaltic nitrate to a solution of 150 g. of magnesium chromate and 5 g. of chromic anhydride in 400 c.c. of water. After six days, 2·9 g. of the compound were obtained in brilliant, dark green, doubly refracting crystals [Found: Co, 12·9; CrO_3, 43·6; NH_3, 14·8. Loss at 95° in 2 hours, 11·2; in 98 hours, 18·2. Loss in a vacuum over sulphuric acid in 2 weeks, 11·4; in 12 weeks, 19·3. (VI) requires Co, 12·8; CrO_3, 43·4; NH_3, 14·8; $6H_2O$, 11·7; $9\frac{1}{2}H_2O$, 18·3; $10H_2O$, 19·5%].

The brown form was only obtained mixed with the green form, from which it could not be separated. The above experiment was repeated with 3 g., 60 g., and 10 g. of the respective compounds in 140 c.c. of water; the deposit which separated after two days was removed, and after 16 days at the summer temperature 1·1 g. of a mixture of brown and green salts were produced, a further quantity being obtained after addition of more of the diaquotetramminecobaltic solution. Under the microscope, the preparation appeared to consist of approximately equal amounts of the two compounds. The total loss of water on dehydration was 12·3% (equivalent to $5{\cdot}8H_2O$), of which 3·6% was evolved very slowly during three months as against 7·7% required for the pure green compound. As the two salts appeared to be present in approximately equal proportions, it may be taken for granted that the whole of the "constitutional" water came from the green component, from which it follows that the brown anion is anhydrous and the formula of the brown salt in the mixture is $(Mg,2H_2O)\left[Co_{4NH_3}^{2CrO_4}\right]_2$. The analysis of the dehydrated mixture gave MgO, 5·3; Co, 15·8; CrO_3, 53·8; NH_3, 18·8. $Mg\left[Co_{4NH_3}^{2CrO_4}\right]_2$ requires MgO, 5·4; Co, 15·9; CrO_3, 53·9; NH_3, 18·4%.

When the green magnesium salt was completely dehydrated and then treated with water at the winter temperature, a brown *hexahydrate* was obtained {Found: total loss at 95°, 13·9. $(Mg,6H_2O)\left[Co_{4NH_3}^{2CrO_4}\right]_2$ requires $6H_2O$, 12·8%}.

The *compound* $Co_2(CrO_4)_3,8NH_3,2\frac{1}{2}H_2O$ separated after four hours as a dark chocolate-coloured powder when the diaquotetramminecobaltic solution from 4 g. of the carbonato-nitrate was added to a solution of 21 g. of sodium chromate in 27 c.c. of water. In a

vacuum over sulphuric acid it lost $1\frac{1}{2}H_2O$ (Found: loss, 4·1, 4·2. Calc.: 4·2%) to give the *monohydrate* [Found: Co, 18·7; CrO_3, 48·2; NH_3, 23·0. $Co_2(CrO_4)_3,8NH_3,H_2O$ requires Co, 19·0; CrO_3, 48·4: NH_3, 22·0%]. A similar preparation from magnesium chromate contained Co, 19·0; CrO_3, 48·5; NH_3, 23·7%.

The Action of Sodium Dichromate on Diaquotetramminecobaltic Salts.—The diaquotetramminecobaltic solution from 5 g. of carbonatotetramminecobaltic nitrate was added to a solution of 150 g. of sodium dichromate dihydrate in 150 c.c. of water and the solution was kept at the summer temperature (below 10° a mixture of compounds is produced). After three days, 3·9 g. of brownish-black crystals were obtained [Found: Co, 11·8; CrO_3, 60·8; H_2O, after 56 days in a vacuum over sulphuric acid, 5·5; NH_3, 15·6. $Co_2(Cr_2O_7)_3,9NH_3,4H_2O$ requires Co, 11·9; CrO_3, 60·5; $3H_2O$, 5·45; NH_3, 15·5%]. When the *compound* was heated to a sufficiently high temperature to expel the fourth molecule of water, general decomposition occurred with evolution of ammonia.

The Action of Ammonium Chromate on Diaquotetramminecobaltic Salts.—The diaquotetramminecobaltic solution from 5 g. of the carbonato-nitrate was added to a solution of 100 g. of ammonium chromate and 5 g. of chromic anhydride in 270 c.c. of water. A slight precipitate was removed by filtration and the solution kept in a warm room. A dark reddish-brown crystalline deposit slowly separated which was only very slightly soluble in water {Found Co, 15·1; CrO_3, 50·6; NH_3, 25·0. $(NH_4)_2CrO_4,\left[Co^{5NH_3}_{CrO_4}\right]_2CrO$ requires Co, 15·0; CrO_3, 50·7; NH_3, 25·9%}.

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XCIX.—*Studies of Electrolytic Polarisation. Part VI Complex Cyanides:* (a) *Silver.*

By Samuel Glasstone.

During the course of an investigation of the rates of dissolution various electrodes under the influence of alternating current, Blanc and Schick (*Z. Elektrochem.*, 1903, **46**, 213; *Z. physik Chem.*, 1903, **9**, 636) observed that with potassium cyanide electrolyte the rate at which a silver electrode dissolved fell rapidly with increasing frequency of the current alternations, even when the frequency was quite small a negligible amount solved. Since the silver ions formed during the anodic pulses [illegible] probably combine readily with cyanide ions to f

complex argentocyanide ions, Le Blanc and Schick suggested that the latter must in turn dissociate rapidly so that silver may be deposited during the cathodic pulses in amounts almost identical with those which dissolved when the electrode was acting as an anode. This view appeared to obtain confirmation from the work of Brunner on the variation of cathodic potential with increasing current density (*C.D.*) during the direct current electrolysis of complex cyanide solutions (*Diss.*, Zurich, 1907; see Foerster, *Z. Elektrochem.*, 1907, **13**, 561). With a solution containing $N/10$-potassium argentocyanide and $N/5$-potassium cyanide it was found that the deposition potential of silver varied only slightly with *C.D.*, and Foerster (*loc. cit.*) explained this observation by the aid of the conclusion of Le Blanc and Schick concerning the rate of dissociation of argentocyanide ions. If the latter come rapidly into equilibrium with free silver and cyanide ions, then the concentration of silver ions in the immediate vicinity of the electrode will not change appreciably during the process of electrodeposition, and hence there should be very little concentration polarisation even at high *C.D.*'s.

In the present paper it is shown that the apparent absence of polarisation, as observed by Brunner (*loc. cit.*), does not necessarily mean that the argentocyanide ion dissociates rapidly, but calcultions made during the course of this work tend to confirm that view. It is also shown that the complex ion may dissociate rapidly even when cathodic polarisation appears to be considerable, because under certain conditions a small decrease in the silver-ion concentration may cause a large change in the electrode potential.

Silver and copper are supposed to behave differently during deposition from complex cyanide solutions, but the observations were made by different authors and not necessarily under the same conditions; thus it is not certain if the solutions were always stirred during the course of cathode-potential measurements made by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345), Höing (*ibid.*, 1916, **22**, 286), and Brunner (*loc. cit.*). Further, in every case, the so-called "direct" method of measurement with the polarising current flowing was used, and this method, especially with solutions of low conductance, is liable to give erroneous results at high *C.D.*'s (see Glasstone, J., 1924, **125**, 250); such errors may mask important changes in the true cathodic potential. Since the published work on the change of deposition potentials of various metals from complex cyanide solutions is of limited scope, a further investigation seemed desirable, especially in view of the importance of such solutions for electroplating and for the electrodeposition of alloys. In this work the commutator-extrapolation method was used for measuring cathode potentials (Glasstone, *loc. cit.*), and the general

conditions were kept as uniform as possible. As part of the comparative studies now being made on the electrochemical properties of solutions containing complex ions, the present paper contains an account of the results obtained during the electrolysis of argentocyanide solutions.

In the course of the present work it became desirable to know how the reversible, or static, potential of a silver electrode against an argentocyanide solution varied with the amount of free cyanide present. For this purpose a rough electrometric titration of silver nitrate with a sodium cyanide solution was performed using a silver indicator-electrode. Treadwell (*Z. anorg. Chem.*, 1911, **71**, 219) and Müller and Lauterbach (*ibid.*, 1922, **121**, 178) have titrated solutions containing potassium cyanide with silver nitrate, but these authors were seeking an accurate end-point for the titration rather than the actual potential values; in the present work the exact end-point was a minor consideration, but the static electrode potential values were important.

In order to make this investigation of argentocyanide solutions reasonably complete, the current efficiencies for metal deposition were determined under various conditions. The influence of certain ions, which are supposed to affect the nature of the silver deposit, has been examined, and the theory of silver deposition discussed.

EXPERIMENTAL.

For most of the work sodium cyanide was used, as a good specimen was available, although previous workers in this field used the potassium salt; reference is made below to the possible differences in behaviour of these two salts. The silver nitrate was a recrystallised commercial product.

Cathode-potential Measurements.—The silver cathodes were generally of about 10 sq. cm. exposed area, and were made by depositing a thick layer of the metal, from an argentocyanide bath, on thin sheets of copper cut to the requisite size; the anode consisted of a short piece of platinum wire. No attempt was made to separate the anode and cathode compartments except in some preliminary work in which measurements were made in an atmosphere of hydrogen; as the results obtained in this way were very similar to those obtained ordinarily, the more complicated procedure was not continued. In order to avoid the possible influence of the nitrate ion acting as a depolariser, the electrolytic solutions were prepared as follows. A known amount of silver nitrate solution was precipitated with the theoretical quantity of cyanide solution; the silver cyanide was filtered off, washed quickly, and dissolved in the requisite amount of standard sodium cyanide solution. For

the preparation of solutions containing equimolar amounts of sodium and silver cyanides, the solution of sodium cyanide was vigorously shaken for some time with excess of silver cyanide; the latter was then filtered off and the clear liquid used. In the measurement of the cathode potentials, the polarising current was increased by stages and held constant for a minute or two before the back *E.M.F.* of the electrode was measured by means of the commutator described previously (J., 1923, **123**, 2926); the results were extrapolated by the method described in connexion with the work on zinc alloys (J., 1927, 642). The reference electrode was in every case a calomel half-element containing a saturated solution of potassium chloride; no allowance was made for diffusion potentials.

Current Efficiencies.—The current efficiencies for silver deposition were investigated in a separate series of experiments, in which a bulk of electrolyte was used sufficient to prevent any appreciable alteration in the concentration of the solution during the process of deposition. Since silver dissolves slowly in cyanide solutions in the presence of oxygen, an allowance was made for this on the weight actually deposited on the cathode; the correction required was never very considerable and was determined by a separate experiment with each solution used.

Unless otherwise stated, experiments were carried out at room temperature (15°). All electrode potential measurements are expressed on the hydrogen scale.

Results.—Table I gives the cathodic potentials (*C.P.*) and percentage current efficiencies (*C.E.*) for silver deposition at various *C.D.*'s from an *N*/10-sodium argentocyanide [$NaAg(CN)_2$] solution (I), and from such a solution containing in addition *N*/10 (II), 3*N*/10 (III), 6*N*/10 (IV) and 9*N*/10-sodium cyanide (V). The results for solutions I and V are plotted in Fig. 1.

TABLE I.

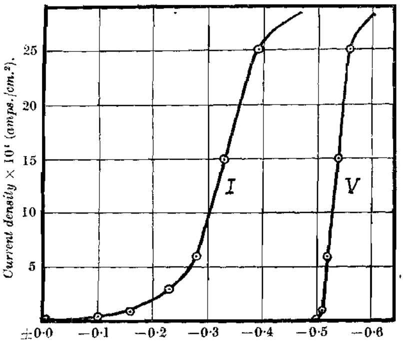
Cathode Potentials and Current Efficiencies.

	I.		II.		III.		IV.		V.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	±0·00	—	−0·33	—	−0·42	—	−0·46	—	−0·50	—
0·5	−0·10	100	−0·34	100	−0·43	100	−0·47	100	−0·51	100
1·0	−0·16	,,	—		—		—		—	
3·0	−0·23	,,	—		—		—		—	
6·0	−0·28	,,	−0·38	100	−0·44	100	−0·48	100	−0·52	100
15	−0·33	,,	−0·41	,,	−0·47	,,	−0·50	,,	−0·54	,,
25	−0·39	,,	−0·49	,,	−0·52	,,	−0·54	,,	−0·58	,,
50	−0·63	75	−0·66	76	−0·64	76	−0·65	78	−0·69	79
100	−1·18	59	−1·26	60	−1·10	62	−1·09	58	−1·12	58
200	−1·42	44	−1·42	44	−1·44	44	−1·45	44	−1·50	43

Electrometric Titration of Silver Nitrate with Sodium Cyanide.—A known volume of *N*/5-silver nitrate solution was placed in a wide tube fitted with a cork carrying a connexion to the silver indicator-

electrode, a tube containing potassium chloride solution for connecting with a standard electrode, and the end of a burette containing $N/5$-sodium cyanide. Definite quantities of the latter solution were added to the silver nitrate, the mixture shaken and the electrode potential of the silver measured. It was found essential to shake the mixture vigorously for some time before taking a measurement, otherwise very misleading results were obtained. As the detailed values are not required for the purposes of the present work, they are omitted, but the variation of electrode

FIG. 1.



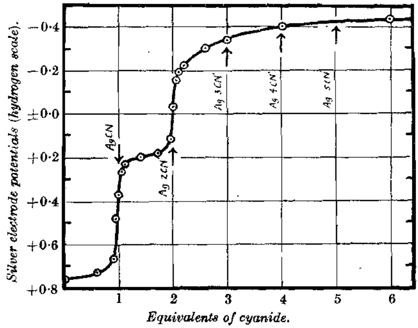
Cathode potentials (volt; on hydrogen scale).

potential with increasing amounts of added cyanide is plotted in Fig. 2. Points corresponding to important ratios of silver cyanide to sodium cyanide are marked on the curve.

A preliminary examination of the *C.D.–C.P.* curves in Fig. 1 would suggest that in a solution of sodium argentocyanide not containing any excess of free cyanide (solution I), there is considerable polarisation during metal deposition, since the cathodic potential increases fairly rapidly with increasing *C.D.* If an appreciable excess of free cyanide is present in the solution, as in (V), however, there is very little variation in the cathode potential for *C.D.*'s below 0·0025 amp./cm.^{2}, and the polarisation during silver deposition appears to be negligible. In the latter solution the free silver-ion concentration, as calculated from the static potential (− 0·5(volt), is apparently much less than in the former solution in which

the potential of a silver electrode is ± 0·0 volt, and hence one would expect the polarisation effects to be reversed. The explanation of this anomaly can be found in the electrometric titration curve (Fig. 2). The potential of a silver electrode in an argentocyanide solution containing no excess of free cyanide is represented by a point near the centre of the second vertical portion of the curve. It is clear, therefore, that any small decrease in the ratio of silver ions to cyanide ions will cause the silver electrode potential to become rapidly more negative until a value of about − 0·3 volt is reached; beyond this point a further decrease in this

Fig. 2.



ratio will result in a gradual increase in the negative potential of the silver until a value of about − 0·55 volt—the static potential in an *N*/2-cyanide solution containing no added silver ions—is reached. During the electrolysis of the argentocyanide solution (I), the deposition of even a small amount of silver on the cathode will cause a slight change in the Ag/CN' ratio in its immediate vicinity, and hence the cathode potential will rise rapidly. As the *C.D.* is increased, the rate of silver deposition is further increased, and the reduction of the Ag/CN' ratio will continue; the cathode potential will thus rise fairly rapidly to − 0·3 volt, and then more slowly to about − 0·5 volt. The *C.D.–C.P.* curve thus gives in this case the impression of considerable polarisation, especially at low *C.D.*'s. With solution (V), which already contains a large excess of cyanide, the static potential is represented by a point on the long horizontal part of the electrometric titration curve; any change in the Ag/CN'

ratio will, consequently, cause very little alteration to the electrode potential. In this case, therefore, although silver ions may be removed from the solution quite rapidly as a result of electro-deposition, no appreciable change occurs in the cathodic potential, and hence there is apparently no polarisation with increasing *C.D.*

In all solutions a condition must be reached in which the silver ions are being deposited on the cathode as fast as they are being brought up to it by diffusion and by other processes; at this point the thin layer of electrolyte in direct contact with the electrode may be regarded as virtually a solution of sodium cyanide containing no silver ions. The electrode potential of silver in such a solution is about − 0·5 volt, and hence, when this cathodic potential is reached, as a result of increasing the *C.D.*, the silver is being deposited at its maximum rate under the particular conditions of the experiment. This occurs in general for a solution containing *N*/10-argentocyanide, with or without excess of free cyanide, at a *C.D.* of 0·0025 amp./cm.^{2}; for an *N*/50-solution the limiting *C.D.* is about 0·0005 (see below). If the *C.D.* is increased beyond this point, then silver ions cannot be brought up to the cathode sufficiently rapidly to satisfy the requirements of the current, and so another process must commence; this is undoubtedly the discharge of hydrogen ions, which, if it occurred reversibly, should set in at a potential of about − 0·65 volt in the solutions under discussion (p_H approx. 11). As a result of hydrogen overvoltage at a silver cathode, however, the gas is not liberated freely until a potential of − 0·85 volt is reached (compare Watts and Brann, *Trans. Amer. Electrochem. Soc.*, 1917, **31**, 303). The cathodic potential of a polarised silver electrode should thus increase rapidly from − 0·55 to − 0·85 volt, and at the same time the current efficiency for metal deposition should fall below 100%. The results obtained in the present work are in complete agreement with these views.

If the *C.D.* is increased beyond the point at which gas evolution commences, it will be seen from Table I that the cathodic potential continues to increase rapidly until a value of about − 1·4 volts is attained; the subsequent increase is, however, not so sudden. The cathodic potentials for hydrogen evolution at a silver electrode in an *N*/2-sodium cyanide solution containing no silver salts have been determined, and the results show that the tendency is exactly the same:

C.D. × 10^4 (amps./cm.^{2})	1	2	3	6	9	15	30
Potential	−0·61	−0·67	−0·94	−1·27	−1·35	−1·43	−1·51

It is not improbable that the rapid increase of potential to − 1· volts may be connected with the discharge of sodium ions to form

a sodium–silver alloy; the current is carried to the cathode almost entirely by these ions and they will accumulate in its immediate vicinity. At high *C.D.*'s some may be deposited, only, however, in the form of an alloy in which the free energy of the sodium is very much below its normal value (compare Haber and Sack, *Z. Elektrochem.*, 1902, **8**, 245; Sack, *Z. anorg. Chem.*, 1903, **34**, 286).

Rate of Dissociation of Argentocyanide Ions.—A consideration of the arguments presented above will show that the actual shape of the *C.D.–C.P.* curve does not give any direct information concerning the rate at which the argentocyanide ion comes into equilibrium with silver and cyanide ions; if the process occurred slowly, the *shape* of the curve would not be altered, but the limiting *C.D.* beyond which the current efficiency drops below 100% would be affected. From the results of the present work it is possible, however, to obtain some idea of the rate of dissociation of argentocyanide ions into simpler ions from which silver deposition can occur.

If the diffusion constant of argentocyanide ions and the thickness of the diffusion layer (compare Glasstone, J., 1925, **127**, 1824) are known, the maximum rate of diffusion of these ions to the cathode can be calculated by the aid of Fick's law. At the ordinary temperature the diffusion constants of most simple salts are between 1·0 and 1·5 (öholm, *Z. physikal. Chem.*, 1904, **50**, 309), and hence we shall probably not be greatly in error if we take the value for the argentocyanide ion as 1·2. The thickness of the diffusion layer in the vicinity of an active electrode has only been determined in a few cases (Brunner, *ibid.*, 1904, **47**, 56; Wilson and Youtz, *J. Ind. Eng. Chem.*, 1923, **15**, 603), but the result obtained by Wilson and Youtz for an unstirred solution, *viz.*, 0·05 cm., may be taken as typical. From these values, and upon the assumption (used by the latter authors) that the concentration of ions at the electrode in the limiting case is zero, it may be calculated that from an *N*/10-argentocyanide solution, assumed to be completely dissociated, the maximum rate of diffusion of these ions to the electrode is 0·0024 g.-equiv. per day per sq. cm. of electrode surface. On the other hand, it may be calculated from the value of the limiting *C.D.*, which is in the present case 0·0025 amp./cm.^{2}, that the rate of silver deposition under these conditions is 0·0022 g.-equiv./day/cm.^{2}. In view of the approximate nature of the calculations, the agreement between the maximum rate of diffusion of argentocyanide ions to the electrode and the rate of silver deposition is very striking, and indicates that the argentocyanide ions come into equilibrium almost instantaneously with simpler ions from which silver is deposited on the cathode.

Influence of Dilution, Temperature, and Stirring.—The cathode-potential and current-efficiency measurements at various *C.D.*'s were repeated, at ordinary temperatures, in solutions (I) and (V) in which was placed a stirrer rotating at 500 r.p.m. A similar series of observations was also made on these solutions at 70°, without stirring. The results of these experiments are given in Table II. In order to determine the effect of dilution, solution (V) was diluted with water to five times its original volume, and series of measurements were made in the stirred and unstirred solutions at ordinary temperatures and in the latter at 70°. The results are given in Table III.

TABLE II.

	Solution stirred.				Solution at 70°.			
	I.		V.		I.		V.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·00	—	−0·50	—	0·02	—	−0·50	—
0·5	−0·05	100	−0·51	100	−0·02	100	−0·51	100
1·0	−0·09	,,	—		−0·06	,,	—	
3·0	−0·15	,,	—		−0·15	,,	—	
6·0	−0·20	,,	—		−0·21	,,	—	
15	−0·25	,,	−0·53	100	−0·26	,,	−0·52	100
25	−0·31	,,	−0·54	,,	−0·29	,,	−0·53	,,
50	−0·38	91	−0·58	90	−0·33	99	−0·54	,,
100	−0·44	73	−0·65	72	−0·60	81	−0·66	83
200	−1·05	60	−1·10	59	−1·10	65	−1·00	68

TABLE III.

Solution (V) diluted five times.

	Temperature 15°.				Temperature 70°.	
	Unstirred.		Stirred.		Unstirred.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·45		−0·45		−0·46	
2	−0·47	100	−0·46	100	−0·47	100
4	−0·48	,,	—			
6	−0·50	85	−0·49	100	−0·48	
8	−0·52	—	—			
10	−0·56	—	—			
15	−0·72	52	−0·52	100	−0·50	
25	−1·09	40	−0·54	85	−0·52	89
50	−1·42	25	−0·91	34	−0·70	55
100	−1·49	23	−1·45	28	−1·25	40
200	−1·55	—	−1·51	—	−1·29	—

Since agitation of the solution increases the rate of diffusion of ions to the electrode, probably as a result of a thinner diffusion layer, it is to be expected that if the electrolyte is stirred the limiting *C.D.* at which the efficiency for metal deposition is 100% will be raised. Under the conditions of the present work, with stirring at the rate of about 500 r.p.m., the limiting *C.D.* has been approx-

imately doubled in the $N/10$-solutions (Tables I and II), but increased about four-fold in the $N/50$-solution (Table III). The effect of raising the temperature to 70° appears to be almost the same as that of the particular type of stirring used in these experiments. Since the argentocyanide ion is already dissociating rapidly *into simpler ions at the ordinary temperature, an increase of temperature* can have relatively little influence in this connexion, and hence the effect of raising the temperature is merely to increase the velocity of ionic diffusion, and possibly to decrease the thickness of the diffusion layer.

For the $N/50$-argentocyanide solution it can be calculated, on the basis of the assumptions stated above, that the maximum rate of *diffusion of the complex ions to the electrode is* 0·00048 g.-equiv./cm.^{2}/day, whilst the rate of deposition of silver at the limiting *C.D.* is 0·00044 g.-equiv. The agreement is again good and confirms the view that the argentocyanide ion dissociates rapidly, even in dilute solution.

Theory of Silver Deposition from Argentocyanide Solutions.—The oldest view concerning the mechanism of silver deposition from cyanide *solutions—one which is still held by many authors—is* apparently due to Hittorf (see Dean and Cheng, *Chem. Met. Eng.*, 1918, **19**, 83; Hughes, "Modern Electroplating," 1923, p. 115). This theory supposes that the alkali-metal ion is first discharged at the cathode, and that the sodium or potassium then reacts with argentocyanide ions to produce silver, thus: $K^{\cdot} + \ominus \longrightarrow K$; $K + Ag(CN)_2' \longrightarrow K^{\cdot} + 2CN' + Ag\downarrow$. According to Dean and Cheng, *since silver is produced as the result of a secondary reaction,* there is no opportunity for the crystals to grow, and so the metal is deposited at random; this is said to account for the production of small crystals and a smooth deposit. The normal deposition potential of the alkali metals is in the vicinity of − 3·0 volts, and even allowing for a considerable reduction of free energy as a result of alloy formation, it is extremely doubtful if there can be any *appreciable discharge of sodium ions at a potential of, say,* − 0·3 *volt,* at which silver deposition from a cyanide solution can occur readily. This theory may therefore be regarded as highly improbable (see also Sanigar, *Rec. trav. chim.*, 1925, **44**, 549). An alternative theory, which has obtained considerable support, is that silver ions produced by the rapid dissociation of argentocyanide ions are directly deposited on the cathode (compare Sanigar, *loc. cit.*), and *that the smooth deposit is due to the minute concentration of* silver ions in the electrolyte. Haber (*Z. Elektrochem.*, 1904, **10**, 433) has pointed out, however, that since the silver-ion concentration is so small, a reasonable rate of metal deposition would

involve electron velocities which must be regarded as impossibly great. Bodländer (*ibid.*, p. 604) then suggested that the complex anion—$Ag(CN)_3''$ is mentioned—takes up a negative charge at the cathode and forms an unstable ion $Ag(CN)_3'''$, which immediately dissociates into $Ag\downarrow$ and $3CN'$. If this mechanism were correct, we should have a case of the deposition of an *anion* on the *cathode!* The possibility of silver deposition occurring through the discharge of a complex kation has not yet been suggested, but this view is not improbable. Transport experiments by Hellwig (*Z. anorg. Chem.*, 1900, **25**, 157) indicated that the double salt $2AgNO_3,AgI$ gave complex kations of the form $(Ag_2I)^{\cdot}$ and $(Ag_3I)^{\cdot\cdot}$ in aqueous solution. The solubility of silver iodide in silver nitrate solution was attributed to the formation of either or both of these complexes. Hellwig found that the solubility of silver cyanide in the nitrate solution is almost the same as that of the iodide, and further, the double salt $2AgNO_3,AgCN$ is known; it appears possible, therefore, that ions such as $(Ag_2CN)^{\cdot}$ and $(Ag_3CN)^{\cdot\cdot}$ may exist in solution. It is now suggested that the presence in an argentocyanide solution of such ions, even if only to the extent of 10^{-4} g.-ion per litre, would account satisfactorily for the deposition of silver from these solutions. The equilibria in the solution would then be $Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN'$, and $2Ag^{\cdot} + CN' \rightleftharpoons (Ag_2CN)^{\cdot}$. At the cathode we should probably have $(Ag_2CN)^{\cdot} + \ominus \longrightarrow Ag\downarrow + Ag^{\cdot} + CN'$. The deposition of silver, according to this view, is a secondary process, and hence the physical nature of the deposits would be explained. Since the complex kation is in equilibrium with silver and cyanide ions, it can be shown that the potential of a silver electrode against the complex ion would be the same as that of a silver|silver-ion electrode in the same solution, and hence there is no difficulty concerning the deposition from a cyanide solution occurring at the reversible potential for silver.

It has already been assumed that the maximum rate at which argentocyanide ions diffuse up to the cathode is proportional to a *C.D.* of 0·0025 amp./cm.^{2} for an $N/10$-solution; at a *C.D.* of 0·02, however, the current efficiency is about 44%, which means that 0·0088 amp./cm.^{2} is being used to deposit silver. This rate is more than three times the maximum value expected; it might, in fact, have been anticipated that the rate of deposition at the higher *C.D.* would have been smaller than at the lower, since in the former case there will be a greater tendency for the argentocyanide ions to migrate away from the cathode. If, as postulated above, the solution contains complex kations which may be brought up, to some extent, by the current from the bulk of the electrolyte to the electrode, especially at high *C.D.*'s, then the increase in the rate of

silver deposition at 0·02 amp. would be expected; this increase may be partly due, however, to the stirring caused by the evolution of hydrogen bubbles.

The presence of complex kations in argentocyanide solutions might account for the abnormal electromotive behaviour of such solutions (compare Bodländer and Eberlein, *ibid.*, 1904, **39**, 226; Frary and Porter, *Trans. Amer. Electrochem. Soc.*, 1915, **28**, 307), and for the fact that no satisfactory stability constant for the $Ag(CN)_2'$ ion could be calculated from the results plotted on Fig. 2 of the present paper.

Influence of Sodium and Potassium Ions.—Although there seemed to be no fundamental reason for supposing that potassium cyanide would behave differently from the sodium salt used in this work, it was desirable to investigate this point in view of the fact that silver deposited from sodium argentocyanide solutions is sometimes regarded as inferior, from the electroplater's standpoint, to that obtained from potassium cyanide solutions (compare Blum and Hogaboom, "Electroplating and Electroforming," 1924, pp. 200 and 292; *Metal Ind.*, 1928, **32**, 214, 235). In all the cases studied, however, there was no appreciable difference in the static potentials of a silver electrode in similar solutions containing either sodium or potassium cyanide, or a mixture of the two salts. There was also no difference in the dynamic potentials under the influence of a polarising current up to a *C.D.* of about 0·002 amp./cm.^{2}, but beyond this point, *i.e.*, in the vicinity of the limiting *C.D.*, slight variations were sometimes observed. Such differences were of the order of 0·02 volt and were probably due to small changes in diffusion rates.

Influence of Carbonates.—It has been found that the addition of carbonates to a silver-plating bath affects the nature of the deposit (compare Sanigar, *Trans. Faraday Soc.*, 1929, **25**, 1), and Hogaboom (Electroplaters' Technical Society, April 18th, 1928) connects such changes with an increase of cathodic potential. In order to verify this, a number of observations were made on solutions of sodium and potassium argentocyanide containing up to 80 g. per litre of the corresponding carbonate. Up to *C.D.*'s of about 0·002 amp./cm.^{2} the carbonate produced no change in the cathode potential, but beyond this point the values were slightly more negative (by 0·02 to 0·03 volt) than in solutions free from carbonate. Exactly the same effect could be produced by adding sodium or potassium *sulphate* to the argentocyanide solution, and so the change in potential is not specific for carbonates, but is connected in some way with the altered cathode environment. It is significant that the *C.D.* used by Hogaboom (*loc. cit.*) would correspond to about

0·0025 *amp./cm.*^{2} *in the present work, when allowance is made for* the difference in concentration of the solutions used.

In technical practice it is general to deposit silver at a *C.D.* of about 0·004 amp./cm.^{2} from an approximately *N*/5-argentocyanide solution, using slight agitation; under these conditions the deposition potential is not likely to be influenced appreciably either by changes in the alkali metal or by the addition of carbonates. If there is any difference in the actual deposits obtained, it is probably due to the fact that the silver crystals grow in different environments: it is well known that the external character of a crystal may vary according to the nature of the solution from which it crystallises. The present author has considered the possibility of the presence of a complex ion of the type $(MAgCN)^{\cdot}$, where M is an alkali metal, in argentocyanide solutions; the discharge of these ions would account for the supposed differences in the deposits obtained from sodium and potassium cyanide solutions, but their existence must for the present be regarded as speculative.

Summary.

(1) The cathode potentials and current efficiencies for silver deposition have been measured in a number of argentocyanide solutions, and the results discussed and explained.

(2) The influence of stirring, temperature, and dilution of the electrolyte has been investigated.

(3) It has been shown that the argentocyanide probably dissociates very rapidly into simpler ions.

(4) The theories of silver deposition from cyanide solutions have been discussed and shown to be unsatisfactory; an alternative theory involving a complex kation is proposed.

(5) The possible influence of sodium, potassium or carbonate ions on the form of the silver electrodeposit is discussed.

UNIVERSITY COLLEGE, EXETER.
THE UNIVERSITY, SHEFFIELD. [*Received, February 25th, 1929.*]

C.—*Studies of Electrolytic Polarisation. Part VIII Complex Cyanides:* (b) *Copper.*

By SAMUEL GLASSTONE.

THE behaviour of a copper electrode in potassium cyanide solutio when submitted to the action of an alternating current is quit different from that of silver: Le Blanc and Schick (*Z. physika Chem.*, 1903, 46, 213; *Z. Elektrochem.*, 1903, 9, 636) found that th

latter did not dissolve to any appreciable extent, but the rate of dissolution of the former only decreased slowly with increasing frequency of current alternations, and was quite considerable even at frequencies of 38,000 per minute. The explanation offered by them was that copper, like silver, ionises during the anodic intervals of the alternating current and readily forms a complex cuprocyanide ion; this, however, unlike the argentocyanide ion, does not come into equilibrium rapidly with its simpler ionic constituents. Hence, during the cathodic pulses the supply of cuprous ions in the vicinity of the electrode will not be sufficient to meet the requirements of the current. Hydrogen ions will then be discharged to an appreciable extent, and more copper will dissolve during the anodic intervals than is replaced during the cathodic periods; the electrode will therefore dissolve under the influence of the alternating current.

Before accepting the views of Le Blanc and Schick concerning the rate of dissociation of the cuprocyanide ion, it is important to remember that copper can dissolve spontaneously in cyanide solutions with the liberation of hydrogen. This has been known for some time (compare Goyder, *Chem. News*, 1894, **69**, 268) and is due to the fact that the concentration of copper ions in a cyanide solution is so low that the electrode potential Cu|KCN is of the order of −1·05 volts, whereas the reversible potential H_2(1 atm.)|KCN is about −0·65 volt. For the same reason, hydrogen will be deposited in preference to copper during the cathodic intervals irrespective of the rate of dissociation of the cuprocyanide ion, provided there is an excess of free cyanide in the electrolyte. It is clear, therefore, that a copper electrode is bound to dissolve to some extent in potassium cyanide solution under the influence of alternating current. Le Blanc and Schick found a decrease in the rate of dissolution with increasing frequency of alternations: this may well be due to the decreased opportunities for the cuprocyanide ions to diffuse away from the electrode, so that appreciable amounts of copper, as well as hydrogen, are deposited during the cathodic pulses. At high frequencies, too, some of the hydrogen deposited during the cathodic intervals will redissolve during the anodic pulses, and so the rate of dissolution of the copper will decrease. It appears, therefore, that the work of Le Blanc and Schick throws no light on the fundamental problem of the rate of dissociation of cuprocyanide ions. In confirmation of this view, it may be mentioned that Brochet and Petit (*Z. Elektrochem.*, 1904, **10**, 916) found that zinc, nickel, and cobalt electrodes behaved like copper when subjected to the action of alternating current electrolysis in cyanide solutions, whereas mercury and cadmium resembled silver. The first three metals, like copper, dissolve spontaneously in cyanide solutions and

liberate hydrogen (compare Goyder, *loc. cit.*), but the other two, like silver, do not react in this manner.

The work of Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) on the variation with *C.D.* of cathodic potential of copper in cuprocyanide solutions at ordinary temperatures, suggested that there was a considerable polarisation during the deposition of the metal; Foerster (*ibid.*, 1907, **13**, 561) correlated this with the supposed slow dissociation of the cuprocyanide ion as suggested by Le Blanc and Schick (*loc. cit.*). Brunner (see Foerster, *loc. cit.*) found that at higher temperatures (*e.g.*, 75°) the cathodic polarisation during copper deposition from cuprocyanide solutions is greatly decreased, and Foerster attributed this to an increased rate of decomposition of the complex ion. It is interesting to note in this connexion, however, that Le Blanc and Schick concluded from their observations that the temperature coefficient of the rate of decomposition of the cuprocyanide complex is very small. More recently, Höing (*ibid.*, 1916, **22**, 286) has determined the deposition potentials at 25° from a solution which was said to be *M*/10 with respect to potassium cuprocyanide, $KCu(CN)_2$, and contained no appreciable excess of free cyanide; it was found in these circumstances that an increase of *C.D.* caused very little cathodic polarisation, and the behaviour was very much the same as that observed by Brunner (*loc. cit.*) during silver deposition. Höing found, however, that the addition of a very small excess of potassium cyanide to the cuprocyanide solution resulted in a considerable polarisation, which he attributed to the presence of the more complex ion $Cu(CN)_3''$ formed by the reaction $Cu(CN)_2' + CN' \longrightarrow Cu(CN)_3''$. According to Foerster's interpretation of the origin of polarisation in the case under discussion, it would be concluded from these results that whilst the $Cu(CN)_2'$ ion dissociated rapidly, the $Cu(CN)_3''$ dissociated only slowly, and even had a tendency to retard the dissociation of the former ion. In the course of the present work it was found that an "*M*/10-solution of $KCu(CN)_2$" probably does not exist at 25°, and that even the solution in which Höing found no appreciable polarisation contains a large proportion of the $Cu(CN)_3''$ ion. In view of the unsatisfactory nature of the position concerning the electrochemical properties and behaviour of cuprocyanide solutions, a more complete investigation seemed desirable, especially as a similar investigation with silver (preceding paper) had yielded interesting results. The conditions were kept as uniform as possible with those existing in the previous work, so the results are comparable. Cathode-potential and current-efficiency measurements were made at various *C.D.*'s, and an electrometric titration of cuprous cyanide with sodium cyanide solution was carried out.

For convenience the results of the latter experiments will be described first.

E X P E R I M E N T A L.

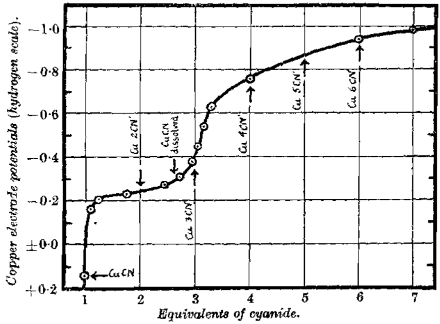
Electrometric Titration of Cuprous Cyanide by Sodium Cyanide.—Kunschert (*Z. anorg. Chem.*, 1904, **41**, 359) and Spitzer (*loc. cit.*) both found that reproducible measurements of copper potentials in cuprocyanide solutions were not easily obtained, and this was confirmed in the present work. During the electrometric titration a current of hydrogen was passed through the liquid; in this way more satisfactory results were obtained with solutions containing an excess of alkali cyanide. Although the general nature of the results was quite reproducible, the actual electrode potential values were not very exact; for the present purpose, however, the latter are not essential.

In accordance with the observations of Spitzer (*loc. cit.*) and Höing (*loc. cit.*), it was found most satisfactory to precipitate cuprous cyanide by adding the correct amount of sodium or potassium cyanide solution to a hot solution of copper sulphate; care was taken to boil off all the cyanogen produced in the reaction. For the electrometric titration, a known amount (about 0·2 g.) of cuprous cyanide thus prepared was transferred to a wide tube together with about 10 c.c. of water and 0·05 g. of sodium sulphate (the latter being used to increase the conductance of the system). The tube was fitted with a cork through which passed a connexion to the copper electrode, a potassium chloride tube for connecting with the calomel half-element used as a standard, the hydrogen lead-in tube, an outlet tube, and the tip of the burette. A standard solution of sodium cyanide was added gradually to the suspension of cuprous cyanide, and the mixture well shaken; the electrode potential of the copper was measured after each addition. Since the actual values are inexact, they need not be given, but some typical results which serve to show the general tendency are plotted in Fig. 1. It may be mentioned that the more limited observations of Spitzer (*loc. cit.*) and of Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 111) are in agreement with those made in the present work.

Although Fig. 1 is a typical electrometric titration curve similar to the one obtained for silver cyanide (see previous paper, Fig. 2), yet a closer examination reveals important differences. Since the break corresponding approximately to Cu : 3CN′ is not very sharp, it appears that although nearly the whole of the copper is present in solution in the form of the $Cu(CN)_3''$ ion, or possibly $[Cu(CN)_3(H_2O)]''$, this is not a very stable ion. On the other hand, the sudden increase of negative potential, *i.e.*, the large reduction in the concentration of cuprous ions, resulting from the addition of

a small amount of alkali cyanide to cuprous cyanide alone, suggests the presence of a stable complex ion, which must presumably be $Cu(CN)_2'$. The titration curve, however, shows no break at a point corresponding to Cu : 2CN', and hence it must be concluded that when cuprous cyanide is dissolved in sodium cyanide both complex ions $Cu(CN)_2'$ and $Cu(CN)_3''$ are formed simultaneously in comparable amounts. If the $Cu(CN)_2'$ ion were completely formed prior to the formation of appreciable amounts of $Cu(CN)_3''$, then we should expect 1 equiv. of cuprous cyanide to be dissolved by 1 equiv. of alkali cyanide, and the titration curve should show a break at this point as in the case of silver cyanide; similarly if

FIG. 1.



only the $Cu(CN)_3''$ ion were formed, then 1 equiv. of the cuprous salt would require 2 equivs. of alkali cyanide for complete dissolution. In practice it is found, however, that about 1·5 equivs. of the latter are actually required, and so it is clear that the resulting solution contains both complex ions in almost equivalent amounts. Kunschert (*loc. cit.*) stated that 2·5 equivs. of alkali cyanide are required to dissolve 1 equiv. of cuprous cyanide, but, as indicated by Spitzer (*loc. cit.*), this is probably a misprint for 1·5.

When 2 equivs. of cyanide ions have been added per equiv. of cuprous cyanide, we may conclude from the curve in Fig. 1 that nearly the whole of the copper is present in the form of the $Cu(CN)_3''$ complex; beyond this point, addition of free cyanide can only have a very gradual influence on the ions present in solution.

The titration of cuprous cyanide with potassium cyanide gives

results almost identical with those given by sodium cyanide, except that a slightly larger proportion of alkali cyanide is required to effect complete dissolution of the precipitate; this fact is probably connected with the limited solubility of $KCu(CN)_2$ (see below).

Höing (*loc. cit.*) claimed to have worked with an *M*/10-solution of $KCu(CN)_2$ at 25°, but in the author's opinion such a solution does not exist at this temperature. The solubility of cuprous cyanide in *N*/10-sodium and potassium cyanides has been determined at 25° and found to be 0·085 and 0·045 g.-equiv. per litre respectively. The value for sodium cyanide tends to confirm the view that both $Cu(CN)_2'$ and $Cu(CN)_3''$ are formed, but with potassium cyanide it would appear that only the latter ion is present. The result is, however, probably connected with the low solubility of the salt $KCu(CN)_2$; Spitzer (*loc. cit.*) gives the value as 0·04 mol. per litre at 25°, but it is probably much less than this, since it seems impossible to prepare a solution of the salt free from cyanide,* and the latter undoubtedly increases the solubility. The presence of both cuprocyanide complexes in the solution of cuprous cyanide in potassium cyanide is suggested by the fact that in *N*/20-solution 1 equiv. of potassium cyanide dissolves 0·65 equiv. of the copper salt; this confirms the view that the smaller relative solubility in the more concentrated potassium cyanide is accounted for by the low solubility of the complex salt. In any case it is clear that the electrolyte used by Höing was probably not an *M*/10-solution of $KCu(CN)_2$ alone, and hence his conclusions regarding the relative rates of dissociation of the two cuprocyanide complexes are not justifiable.

At higher temperatures the solubility of cuprous cyanide in alkali cyanides is increased, presumably because there is less tendency for the $Cu(CN)_3''$ complex to be formed as the temperature is raised. When the solution is cooled, cuprous cyanide, and, particularly in the case of potassium, some complex salt are precipitated.

Cathode-potential and Current-efficiency Measurements.—The electrolytic solutions were prepared by dissolving cuprous cyanide, precipitated as described above, in the requisite volume of standard sodium cyanide solution. During the course of the work it was found that the presence of a small concentration of sulphate ions (*e.g.*, *N*/10) had no appreciable influence on any of the measurements made; hence the alkali cyanide solution was generally added to the cuprous cyanide suspension without filtering the latter. The so-called "*N*/10-cuprocyanide" solution was made by saturating *N*/10-sodium cyanide solution with cuprous cyanide and filtering off the excess of the solid; the clear liquid apparently contained

* Compare Bassett and Corbet, J., 1924, **125**, 660.

0·06 g.-ion of $Cu(CN)_2'$ and 0·02 g.-ion of $Cu(CN)_3''$ per litre. Cathodic potentials were measured at increasing *C.D.*'s by the method described in the previous paper. The determination of current efficiencies presented some difficulty owing to the tendency of copper to dissolve in cyanide solution, particularly in the presence of air. Separate experiments were made in order to determine the normal loss in weight of the copper electrode in each of the solutions used in this work, and a correction was applied to the actual weight of the deposit (compare Field, *Trans. Faraday Soc.*, 1909, **5**, 172). The rate of dissolution was greatest in those solutions in which the current efficiency was least, and so the results for solutions containing an excess of free cyanide, especially at high *C.D.*'s, can only be regarded as approximate. In some instances, in fact, the cathode actually lost in weight during the electro-deposition, because it was dissolving spontaneously faster than it was being deposited. Owing to such difficulties as these, the current efficiencies were only determined down to a *C.D.* of 0·0004 amp./cm.^{2}.

Unless otherwise stated, experiments were carried out at room temperature (15°). All electrode-potential measurements are expressed on the hydrogen scale.

Results.—Table I gives the cathode potentials (*C.P.*) and percentage current efficiencies (*C.E.*) for deposition of copper as a univalent metal, at different *C.D.*'s from the so-called "*N*/10-cuprocyanide" solution (I), and from four other solutions which can be represented by the general formula *N*/10-[CuCN,*n*KCN], where *n* is equal to 2 (II), 3 (III), 5 (IV) and 7 (V). The results of the cathode-potential measurements in solutions I and II have been plotted in Fig. 2.

TABLE I.

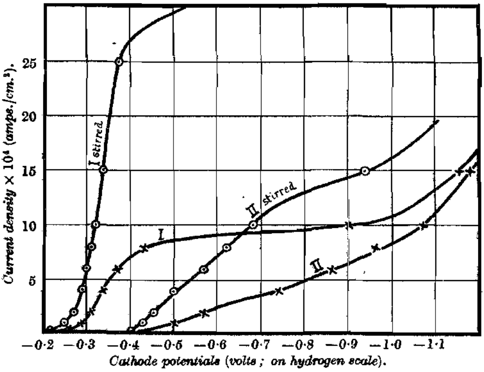
Cathode Potentials and Current Efficiencies.

C.D. × 10^4 (amps./cm.^{2}).	I. *C.P.*	I. *C.E.*	II. *C.P.*	II. *C.E.*	III. *C.P.*	III. *C.E.*	IV. *C.P.*	IV. *C.E.*	V. *C.P.*	V. *C.E.*
—	−0·22	—	−0·40	—	−0·75	—	−0·94	—	−1·00	—
1·0	−0·29	—	−0·50	—	−0·77	—	−0·98	—	−1·02	—
2·0	−0·31	—	−0·57	—	−0·79	—	−1·01	—	−1·05	—
4·0	−0·34	100	−0·74	65	−0·96	62	−1·08	50	−1·08	43
6·0	−0·39	81	−0·86	44	−1·05	36	−1·15	26	−1·15	17
10	−0·90	—	−1·07	—	−1·20	—	−1·28	—	−1·28	—
15	−1·13	47	−1·18	32	−1·27	21	−1·32	13	−1·32	9
25	−1·32	33	−1·26	28	−1·34	13	−1·36	6	−1·36	5
50	−1·38	28	−1·37	22	−1·39	11	−1·40	3	−1·40	1·7
100	−1·41	22	−1·41	18	−1·43	9	−1·43	1·5	−1·43	0·4

A comparison of the results given in Table I with those obtained for argentocyanide solutions (see previous paper) suggests that the general behaviour is entirely different in the two cases. On the whole, there is much more polarisation in the cuprocyanide solutions the current efficiencies for metal deposition are considerably lowe

and very much affected by an increase in the free cyanide content of the electrolyte. At first sight it would appear, therefore, that the conclusions of Le Blanc and Schick (*loc. cit.*) and of Foerster (*loc. cit.*) concerning the slow decomposition of the cuprocyanide complex are correct. There are, however, two important differences in the behaviour of copper and silver in cyanide solutions that must be taken into consideration. First, an examination of the curve in Fig. 1 shows that any increase of the CN′/Cu ratio above 2 to 1 causes the copper electrode potential to increase at first gradually from —0·2 to —0·35 volt, and then more rapidly to —0·9 volt; the electrode potential change is, therefore, much greater than in

FIG. 2.



the case of silver. Secondly, the reversible potential for hydrogen evolution in a $N/10$-cyanide solution is about —0·65 volt, and hence in all solutions in which the ratio CN′/Cu exceeds 3·4 the reversible copper potential is more negative. In such solutions hydrogen evolution can thus occur simultaneously with copper deposition, and the current efficiency for the latter cannot be 100%. Although the hydrogen overvoltage at copper raises the actual potential for hydrogen evolution to —0·85 volt, yet during the course of electro-deposition such a potential is soon reached as a result of a small decrease in the cuprous-ion concentration.

The divergence of the current efficiency from 100% is not necessarily due to simultaneous hydrogen evolution only; there is evidence

that sodium cyanide can act as a depolariser at a copper cathode, possibly with the resulting formation of methylamine, and hence some of the current may be employed in this reduction process.

In solution I we should expect the cathode potential to increase steadily from −0·22 to about −0·4 volt, whilst the current efficiency remains at 100%; beyond this point the potential should rise rapidly to about −1·0 volt with the simultaneous evolution of hydrogen and lowering of current efficiency. This is in agreement with the actual results (see Table I). In solution II the reversible potential is already −0·4 volt, and hence the cathodic potential should increase rapidly from the beginning as the *C.D.* is increased; the results in Table I and the curve in Fig. 2 show this to be the case. The current efficiency, as would be expected, even at the lowest *C.D.* investigated is below 100%. In the other solutions used in this work hydrogen discharge can occur from the commencement; in fact, the cathode potentials for solution V are very similar to those for hydrogen evolution at a copper cathode in an *N*/2-sodium cyanide solution.

Rate of Dissociation of Cuprocyanide Ions.—Since the change of CN′/Cu ratio in an electrolyte soon brings the potential of the copper cathode into the region of hydrogen evolution, it is not possible to apply directly the criterion of diffusion velocity which was used in the case of silver; a modified test is, however, possible. If the rate of diffusion of the cuprocyanide ion $Cu(CN)_2'$ is assumed to be the same as that of the $Ag(CN)_2'$ ion, and we assume that the former ion, like the latter, dissociates *rapidly*, then the maximum *C.D.* at which the metal deposition efficiency is 100% should be about 0·0025 amp./cm.^{2} (see previous paper). In solution I, however, this maximum is reached at 0·0005 amp./cm.^{2}, when the cuprocyanide-ion concentration in the vicinity of the electrode must be at least three-fourths of its value in the bulk of the electrolyte. It might appear, therefore, that the cuprocyanide ions are present in sufficient concentration, but that they dissociate slowly into the simpler ions from which copper deposition can occur. If this were the case, then stirring of the electrolyte should have very little influence on the cathode potentials and the current efficiencies. Increase of temperature, on the other hand, might be expected to increase the rate of dissociation of the complex ions, and hence would lead to less polarisation and higher efficiencies. In order to test these points, a number of cathode-potential and current-efficiency measurements were made in solutions I and II whilst they were stirred mechanically at the rate of 500 r.p.m., and also in the same solutions at a temperature of 70°, without stirring. The results obtained are given in Table II; the cathode-potential measurements in the stirred

solutions are plotted in Fig. 2 for comparison with those obtained in the unstirred solutions at the same temperature.

TABLE II.

$C.D. \times 10^4$ (amps./cm.^{2}).	Solution stirred.				Solution at 70°.			
	I.		II.		I.		II.	
	C.P.	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·22	—	−0·40	—	−0·22	—	−0·38	—
1·0	−0·25	—	−0·43	—	−0·24	—	−0·40	—
2·0	−0·27	—	−0·46	—	−0·26	—	−0·43	—
4·0	−0·29	100	−0·50	100	−0·28	100	−0·45	100
6·0	−0·30	,,	−0·57	87	−0·30	,,	−0·47	,,
10	−0·32	,,	−0·68	—	−0·39	,,	−0·52	—
15	−0·34	,,	−0·94	64	−0·45	96	−0·58	89
25	−0·47	85	−1·12	44	−0·85	78	−0·80	71
50	−1·13	59	−1·23	33	−1·11	63	−0·98	62
100	−1·33	38	−1·32	28	−1·29	43	−1·25	48

The values in Table II show that stirring of the electrolyte has a very considerable effect in reducing cathodic polarisation and *increasing the current efficiency, especially in solution I*; *the results*, therefore, are opposed to the view that the cuprocyanide ions dissociate slowly, unless the assumptions concerning the rate of diffusion of these ions are incorrect. The observations are, however, in harmony with the rate of dissociation being rapid; in this case stirring would be expected to retard the normal increase of the CN′/Cu ratio, and hence the rise of cathode potential at about −0·4 volt, *with its corresponding decrease* of *current efficiency*, should occur at a higher *C.D.* This change of potential is bound to occur as soon as the ratio CN′/Cu approaches 3, and so the limiting *C.D.* for 100% efficiency will be below that obtained in *N*/10-argentocyanide solutions. Although cuprocyanide solution I and argentocyanide solution I are not strictly comparable, yet the fact that the limiting *C.D.*'s in stirred solutions are 0·0025 and 0·005 amp./cm.^{2}, respectively, suggests that there is really no essential difference in behaviour: both complex ions probably dissociate rapidly. The influence of stirring is also quite marked in solution II, although the limiting *C.D.* for 100% efficiency is raised only to 0·0005 amp./cm.^{2}; since the static potential of copper in this solution is already −0·4 volt, it is clear that the rapid rise of cathode potential cannot be long delayed even by stirring.

The effect of increasing the temperature is also to decrease the polarisation and to increase the current efficiency; with solution I, as in the corresponding case of silver, the result of raising the temperature to 70° is also the same as stirring under the particular conditions used in this work. This is further confirmation of the

view that cuprocyanide ions do not dissociate slowly, for if they did the influence of temperature would be far greater than that of stirring. In solution II, *an increase of the temperature to* 70° *improves the current efficiency somewhat more than does stirring*, although the difference is not considerable; this may be connected with the fact, already mentioned, that an increase of temperature tends to retard the formation of the $Cu(CN)_3''$ complex, which probably diffuses more slowly than the $Cu(CN)_2'$ ion.

All the work described above was carried out with sodium cyanide solutions, but as other authors have used potassium cyanide some experiments were made with the latter for purposes of comparison. The electrolyte corresponding to solution I showed slight differences on account of the lower solubility of cuprous cyanide in potassium cyanide (see p. 707); the static potential of copper in this solution was −0·27 volt, as compared with −0·22 volt in the sodium cyanide solution. The cathodic potentials were very similar, but the current efficiencies were, naturally, somewhat lower in the potassium cyanide solution. With the other solutions the results were in general very similar for both cyanides; small differences in cathodic potential were probably due to the difficulty of obtaining concordant results for copper potentials in cyanide solutions.

Theory of Copper Deposition from Cuprocyanide Solutions.—Although the theory of alkali-metal discharge as a primary process in the electrodeposition of copper from cuprocyanide solutions has not been definitely suggested, yet it would seem to be as applicable to this case as to argentocyanide solutions; the same objections, however, apply to both cases (see previous paper). The theory generally accepted is that copper is deposited from cuprous ions produced by the dissociation of cuprocyanide ions, but the objection raised by Haber applies to this case as it does to silver (*Z. Elektrochem.*, 1904, **10**, 433). Foerster ("Elektrochemie Wässeriger Lösungen," 1922, p. 299, footnote), following Bodländer (*Z. Elektrochem.*, 1904, **10**, 604), has suggested that the *anion* $Cu(CN)_4'''$ is discharged at the *cathode*; this, however, seems very improbable. Although there is no independent evidence for the existence of the complex kations $(Cu_2CN)^{\cdot}$ and $(Cu_3CN)^{\cdot\cdot}$, yet it is not improbable that a small concentration of such ions, as postulated in the case of silver (p. 700), is present in cuprocyanide solutions. The discharge of these ions at the cathode would yield copper, in a finely crystalline form, as a secondary product. As soon as the complex ions were removed they would be regenerated from cuprocyanide ions as a result of the displacement of the equilibria $(Cu_2CN)^{\cdot} \rightleftharpoons 2Cu^{\cdot} + CN'$; $Cu(CN)_2' \rightleftharpoons Cu^{\cdot} + 2CN'$; $Cu(CN)_3'' \rightleftharpoons Cu^{\cdot} + 3CN'$.

Summary.

(1) The evidence for the slow dissociation of the cuprocyanide ion is discussed and shown to be inconclusive.

(2) Electrometric titration of cuprous cyanide and solubility measurements in alkali cyanide solutions show that the complex ions $Cu(CN)_2'$ and $Cu(CN)_3''$ can both exist.

(3) The cathode potentials and current efficiencies for copper deposition have been measured in a number of cuprocyanide solutions, and the results discussed.

(4) The effects of raising the temperature and of stirring the electrolyte have been investigated, and shown to be in harmony with the view that the cuprocyanide ion dissociates rapidly.

(5) The difference in behaviour of copper and silver in complex cyanide solutions is shown to be connected with the fact that a small increase in the ratio of cyanide to metal ions in the case of copper raises the electrode potential to a point at which the evolution of hydrogen is possible.

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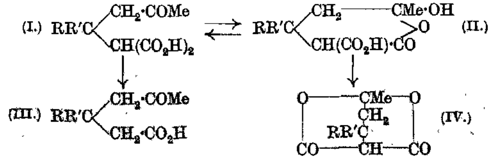
CI.—*Studies in Keto-lactol Tautomerism. Part II. Influence of the* cyclo*Hexane Ring on the Tautomeric Character of* cyclo*Hexane*-1-*acetone*-1-*malonic Acid, a Comparison with* cyclo*Pentane*-1-*acetone*-1-*malonic Acid, and Synthesis of the Corresponding δ-Keto-monobasic Acids.*

By MUHAMMAD QUDRAT-I-KHUDA.

IN Part I (this vol., p. 201) it was suggested that in the liquid state α-carboxy-γ-acetyl-ββ-dimethylbutyric acid exists both in the keto-form (I) and in the carboxy-lactol form (II), which decompose at 130—140° and give the keto-monocarboxylic acid (III) and the dilactone (IV) respectively (R = R′ = Me).



The properties of cyclo*hexane-1-acetone-1-malonic acid* (I; RR′ = $C_5H_{10}>$) and cyclo*pentane-1-acetone-1-malonic acid* (I; RR′ = $C_4H_8>$) and the influence of the *cyclo*hexane and *cyclo*pentane rings on their tautomerism have now been examined.

Evidence has been accumulated which shows that the forcing apart of two of the valencies of a spiran carbon atom due to its inclusion in a *cyclo*hexane ring causes the other two valencies to come closer together: *cyclo*hexane*spirocyclo*propane-1 : 2-dicarboxylic acid, therefore, is more stable than the corresponding *gem*-dimethyl compound (V; RR′ = $C_5H_{10}>$ and Me_2, respectively) (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1091; compare also Kon, J., 1922, **121**, 514; Ingold and Gane, J., 1928, 2268). On the other hand, the angle included by two of the valencies of a carbon atom in a *cyclo*pentane ring is almost equal to the normal tetrahedral angle, and consequently the influence exerted by this ring is comparable with that of *gem*-dimethyl groups (compare, *e.g.*, Becker and Thorpe, J., 1920, **117**, 1579; Dickens, Kon, and Thorpe, J., 1922, **121**, 1496; Lanfear and Thorpe, J., 1923, **123**, 1683; Ingold, Lanfear, and Thorpe, *ibid.*, p. 3140). The behaviour of *cyclo*hexane- and *cyclo*pentane-1-acetone-1-malonic acids supports these views: *cyclo*hexane-1-acetone-1-malonic acid, owing to the proximity of the carbonyl and the carboxyl groups (compare Ingold and Gane, *loc. cit.*), exhibits pronounced tautomeric behaviour, whereas the *cyclo*pentane analogue resembles the *gem*-dimethyl compound in its general reactions.

(V.) $RR'C<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$ $\qquad$ $RR'C<\begin{matrix}CH_2\cdot CMe(OH)\\ CH(CN)—CO\end{matrix}>NH$ (VI.)

The carboxy-lactol forms (II) of the two acids could not be isolated. They are δ-hydroxy-acids, and apparently it is through them, by the loss of a molecule of water, that transformation of the acids (I) into the *dilactones* (IV) takes place: the *cyclo*hexane acid undergoes the conversion when heated in an organic solvent for some time, but the *cyclo*pentane acid requires the assistance of a dehydrating agent.

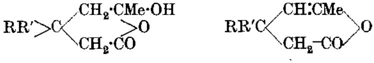
The best method for the preparation of *cyclo*hexane- and *cyclo*pentane-1-acetone-1-malonic acids is the alkaline hydrolysis of the condensation products of *cyclo*hexenylacetone and *cyclo*pentenylacetone, respectively, with sodiocyanoacetamide in hot alcoholic solution (the condensation could not be effected with a small quantity of sodium ethoxide as in the case of mesityl oxide; this vol., p. 205): the cyclo*hexane*- and cyclo*pentane*-spiro-3-*hydroxy-6-cyano-3-methyl-5-piperidones* (VI; RR′ = $C_5H_{10}>$ and $C_4H_8>$

respectively) obtained, on hydrolysis with concentrated aqueous potash, yield the desired acids as the sole products.

When treated with alcoholic hydrogen chloride, *cyclo*pentane-1-acetone-1-malonic acid gives the normal *keto-ester* (formula as I), but the *cyclo*hexane acid gives a mixture of its *keto-ester* with a substance, probably the dilactone, which is very difficult to purify : the pure keto-ester, however, can be obtained from the silver salt. The keto-esters have the normal configuration, since they give characteristic *semicarbazones*.

Like the *gem*-dimethyl acid, *cyclo*hexane- and *cyclo*pentane-1-acetone-1-malonic acids in the liquid state exist each as an equilibrium mixture of the keto and the lactol form (I $\rightleftharpoons$ II). The composition of the equilibrium mixture is deduced from the quantities of the decomposition products of the two forms, namely, the keto-monobasic acid (III) from the keto-form and the dilactone (IV) from the lactol form : the *cyclo*hexane acid yields 68—70%, and the *cyclo*pentane acid 47—48%, of dilactone; the rest of the acid decomposes into and is isolated as keto-monobasic acid. The constitutions of the two keto-monobasic acids have been established by the syntheses of their *methyl* esters from the acid chlorides of the corresponding diacetic acids and zinc methyl iodide.

The keto-monobasic acids were examined for evidence of their existence in the lactol form (VII). It was expected that from *cyclo*hexane-1-acetone-1-acetic acid, at least, it might be possible to get an ethoxy-lactone (VII with OEt in place of OH). The reaction with alcoholic hydrogen chloride, however, proceeded in a different direction, giving mainly Norris and Thorpe's *cyclo*hexane-*spirocyclo*hexane-3 : 5-dione (J., 1921, **119**, 1205) and a small quantity of the keto-ester. Esterification of *cyclo*pentane-1-acetone-1-acetic acid gave, as in the case of the *gem*-dimethyl analogue, mainly the keto-ester.

(VII.)  (VIII.)

Methyl *cyclo*hexane- and *cyclo*pentane-1-acetone-1-acetate, when heated with alcoholic sodium ethoxide solution, are converted into *cyclo*hexane- and *cyclo*pentane-*spirocyclo*hexane-3 : 5-dione (Norris and Thorpe, *loc. cit.*), respectively. The keto-acids of the general formula (III), when treated with acetyl chloride, react, however, in their lactol form (VII) witb tbe production of unsaturated lactones (VIII) by loss of a molecule of water : the *cyclo*hexane acid undergoes the change at the ordinary temperature, but the *cyclo*pentane analogue requires heating on a steam-bath.

The effect of bulky substituents on the tautomerism of such δ-ketonic acids will be discussed in a future communication.

EXPERIMENTAL.

The condensation of cyanoacetamide with *cyclo*hexenylacetone or *cyclo*pentenylacetone was effected by heating the suspension of the sodio-derivative, obtained by adding cyanoacetamide (1 mol.) in 1000 c.c. of hot absolute alcohol to a solution of sodium (1 atom) in 350 c.c. of hot absolute alcohol, with the unsaturated ketone (1 mol.) on the steam-bath for 6 hours, the sodiocyanoacetamide dissolving and the sodio-derivative of the condensation product separating. The alcohol is then distilled off, the residue dissolved in water, any unchanged ketone extracted with ether, and the solutiou acidified with cold hydrochloric acid : the condensation product crystallises. A few grams more are obtained when the mother-liquor is made just alkaline with sodium carbonate solution and concentrated on the steam-bath.

cyclo*Hexane Series.*

cyclo*Hexane*spirocyclo-3-*hydroxy*-6-*cyano*-3-*methyl*-5-*piperidone* (VI; $RR' = C_5H_{10}>$).—When *cyclo*hexenylacetone (b. p. 90°/15 mm., $d_{4°}^{16·2°}$ 0·9404, $n_D^{16·2°}$ 1·47751; prepared by Wallach's method, *Annalen*, 1912, **394**, 376, and purified hy two distillations) (27·6 g.) is condensed with cyanoacetamide (16·8 g.) and sodium (4·6 g.) as described above, cyclo*hexane*spirocyclo-3-*hydroxy*-6-*cyano*-3-*methyl*-5-*piperidone* is obtained (35 g.). It crystallises well from methyl alcohol and melts with charring at 258° (Found : C, 65·4; H, 8·5; N, 12·7. $C_{12}H_{18}O_2N_2$ requires C, 64·9; H, 8·1; N, 12·6%). It is unaffected by hot dilute caustic soda solution, is appreciably soluble in caustic alkalis and in dilute acids, and dissolves in hot alcohol or acetic acid, but is insoluble in ether, benzene, or chloroform.

cyclo*Hexane*-1-*acetone*-1-*malonic Acid* (I).—The preceding *spiro*-compound (25 g.) is heated with potassium hydroxide (25 g.) in 100 c.c. of water for 28 hours and the solution is cooled, diluted, extracted with ether to remove any neutral product, and acidified in the cold. The oil obtained, after being dried in ether and recovered, slowly solidifies in a vacuum desiccator (yield, 25 g.). After being triturated with cold benzene and dried in a vacuum desiccator for several days, the *acid* melts at 116° and decomposes at about 118° (Found : C, 59·2; H, 7·6; *M*, by titration, 242. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%; *M*, 242). When crystallised from hot benzene or chloroform, or precipitated from cold ethyl acetate solution by petrol, it invariably contains a gummy impurity. The acid is almost insoluble in cold benzene, but after it has been heated with an excess of this solvent (or high-boiling organic solvents) on the

steam-bath for 45 minutes, the dilactone described below is the only product that can be isolated on evaporation of the solvent. The acid, on treatment with semicarbazide acetate in aqueous methyl-alcoholic solution, gives a semicarbazone mixed with some of the dilactone. The *semicarbazone*, after treatment with cold benzene and repeated crystallisation from methyl alcohol, has m. p. 183° (decomp.) (Found: C, 52·1; H, 7·4. $C_{13}H_{21}O_5N_3$ requires C, 52·2; H, 7·0%).

The ethyl ester. The dry silver salt (15 g.) is heated under reflux over-night with ethyl iodide (10 c.c. in 60 c.c. of alcohol); the filtered solution is then concentrated under reduced pressure. The *ester*, isolated in the usual way, is a colourless liquid, b. p. 192°/14 mm., $d_{4^\circ}^{18.5^\circ}$ 1·0681, $n_D^{18.5^\circ}$ 1·46984, whence $[R_L]_D = 77{\cdot}3$ (calc. for the normal ester, 77·2) (Found: C, 64·6; H, 9·0. $C_{16}H_{26}O_5$ requires C, 64·4; H, 8·7%). It gives a *semicarbazone*, m. p. 104° after crystallising from ethyl acetate–light petroleum (Found: C, 57·3; H, 8·3. $C_{17}H_{29}O_5N_3$ requires C, 57·4; H, 8·2%). When the acid is esterified with alcohol and a mineral acid, an ester is obtained which gives the same semicarbazone as the above and thus appears to be the same normal ester, but its physical properties indicate that it is not quite pure.

Behaviour of cyclo*Hexane*-1-*acetone*-1-*malonic Acid on Heating. Formation of the Dilactone* (IV) *and* cyclo*Hexane*-1-*acetone*-1-*acetic Acid* (III).—The acid (5 g.) is heated for 5—6 hours at 130—140°, the melt cooled and dissolved in benzene, and the benzene solution extracted with dilute aqueous sodium carbonate, dried, and evaporated. The *dilactone* thus obtained (3·13 g., representing 68% of the keto-dibasic acid) has m. p. 141° after crystallising from methyl alcohol (Found: C, 64·1; H, 7·5. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%). It is the sole product obtained when the *cyclo*hexane acid is treated with concentrated hydrochloric acid or a dehydrating agent, and gives this acid on being hydrolysed with hot dilute caustic alkali solution. It is very soluble in benzene, chloroform, and ethyl acetate, but sparingly soluble in ether and cold alcohol.

The sodium carbonate extract on acidification gives an oil (1·3 g.) which gradually crystallises. After recrystallisation from petroleum (b. p. 60—80°), it melts at 73°, alone or mixed with the cyclo*hexane*-1-*acetone*-1-*acetic acid* (III) described below (Found: C, 66·3; H, 9·3. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%).

Several experiments on heating were carried out with different quantities of the acid. The percentage of the dibasic acid converted into the dilactone was always 68—70% and the other product was the keto-monobasic acid (III).

Synthesis of Methyl cyclo*Hexane*-1-*acetone*-1-*acetate*.—*cyclo*Hexane-

1 : 1-diacetic anhydride [readily prepared by heating the acid (Kon and Thorpe, J., 1919, **115**, 693; compare also Thole and Thorpe, J., 1911, **99**, 445) with acetic anhydride] (91 g.) is heated with methyl alcohol (40 c.c.) for 4 hours on the steam-bath and the alcohol is then removed by evaporation. The acid ester obtained is purified through the sodium salt, but cannot be made to solidify (Found for the *silver* salt: Ag, 33·8. $C_{11}H_{17}O_4Ag$ requires Ag, 33·6%). The acid ester (30 g.) is heated with thionyl chloride (15 c.c.) on the steam-bath, the excess of thionyl chloride removed under diminished pressure, and the acid chloride added to a cold benzene solution of zinc methyl iodide (compare this vol., p. 207). The keto-ester obtained is converted into the *semicarbazone*, m. p. 137° after crystallising from methyl alcohol (Found: C, 57·7; H, 9·0. $C_{13}H_{23}O_3N_3$ requires C, 57·9; H, 8·5%). *Methyl* cyclo*hexane*-1-*acetone*-1-*acetate*, regenerated from this, has b. p. 152°/18 mm., $d_4^{20.4°}$ 1·0363, $n_D^{20.4°}$ 1·46748, whence $[R_L]_D = 56{\cdot}81$ (calc. for the normal ester, 57·08) (Found: C, 67·5; H, 9·8. $C_{12}H_{20}O_3$ requires C, 67·8; H, 9·5%). On being heated with the required amount of alcoholic sodium ethoxide it is converted completely into *cyclo*hexane*spirocyclo*hexane-3 : 5-dione, which crystallises from benzene in needles, m. p. 169—170° (Norris and Thorpe, *loc. cit.*).

cyclo*Hexane*-1-*acetone*-1-*acetic Acid*.—The keto-ester just described (30 g.) is heated with potassium hydroxide (20 g.) in 20 c.c. of water and 100 c.c. of methyl alcohol on the steam-bath for 12 hours, the alcohol removed under diminished pressure, and the residue diluted with water, extracted with ether, and acidified with hydrochloric acid. The oil obtained, isolated by means of ether, slowly solidifies, and contains *cyclo*hexane-1-acetone-1-acetic acid and a small amount of *cyclo*hexane-1 : 1-diacetic acid. Separation is effected by hot petroleum (b. p. 60—80°), in which the former alone is soluble. On removal of the solvent the keto-acid is obtained pure, m. p. 73° Norris gives m. p. 67° (J., 1926, 248) (Found: C, 66·3; H, 9·4% *M*, by titration, 194). The *semicarbazone*, crystallised from methy alcohol, melts at 185° (Found: C, 56·6; H, 8·6. $C_{12}H_{21}O_3N$ requires C, 56·5; H, 8·2%).

Action of Acetyl Chloride on cyclo*Hexane*-1-*acetone*-1-*acetic Acid*.— A mixture of the acid (5 g.) and an excess of acetyl chloride (8 c.c is kept at the ordinary temperature for 12 hours, hydrogen chloric being given off, and is then treated with water and extracted wit ether. The extract is washed with sodium carbonate solution ar with water, dried, and distilled. The neutral, mobile, colourle liquid obtained has b. p. 144°/17 mm., $d_4^{20°}$ 1·0533, $n_D^{20°}$ 1·495 whence $[R_L]_D = 49{\cdot}85$ (calc., 49·70) (Found: C, 72·7; H, 9

$C_{11}H_{16}O_2$ requires C, 73·3; H, 8·8%). The unsaturated *lactone* (VIII) is hydrolysed by alcoholic potash, giving the keto-monocarboxylic acid, m. p. 73°.

cyclo*Pentane Series.*

The compounds of this series (RR′ = C_4H_8> in the formulæ) are prepared in substantially the same way as the corresponding compounds of the *cyclo*hexane series.

cyclo*Pentane*spiro*cyclo-3-hydroxy-6-cyano-3-methyl-5-piperidone* (VI) (18 g.), prepared from *cyclo*pentenylacetone (26 c.c.), cyanoacetamide (16·8 g.), and sodium (4·6 g.), crystallises best from dilute acetic acid and melts at 282° (Found: C, 63·3; H, 8·1. $C_{11}H_{16}O_2N_2$ requires C, 63·4; H, 7·7%). It resembles the *cyclo*hexane analogue in solubility.

cyclo*Pentane-1-acetone-1-malonic acid* (I) separates from hot chloroform–petroleum in characteristic, half-pyramid-shaped crystals, m. p. 106°, decomp. near 130° (Found: C, 57·8; H, 7·4; *M*, by titration, 228. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0%; *M*, 228). It is practically unaffected by ordinary hot solvents, but is transformed into the dilactone (IV) by concentrated hydrochloric acid or any dehydrating agent. The *semicarbazone*, after crystallising from methyl alcohol, melts at 177° (Found: C, 50·6; H, 6·8. $C_{12}H_{19}O_5N_3$ requires C, 50·5; H, 6·7%). When esterified with alcohol and hydrogen chloride, the acid gives what appears to be the normal *ethyl* ester, b. p. 179°/13 mm., $d_{4^\circ}^{18^\circ}$ 1·0767, $n_D^{18^\circ}$ 1·4632, whence $[R_L]_D$ = 72·68 (calc. for the normal ester, 72·78) (Found: C, 63·2; H, 8·7. $C_{15}H_{24}O_5$ requires C, 63·3; H, 8·4%). The ester yields readily a *semicarbazone* which melts at 109° after crystallising from ethyl acetate and light petroleum (Found: C, 56·6; H, 8·3. $C_{16}H_{27}O_5N_3$ requires C, 56·3; H, 7·9%).

Behaviour of cyclo*Pentane-1-acetone-1-malonic Acid on Heating.*—When the acid (5 g.) is heated at 140—150° for 5 hours, and the product separated into neutral and acidic portions, 2·1 g. of the *dilactone* (IV), representing about 47% of the total dibasic acid, is obtained. After crystallising from methyl alcohol, it melts at 139° (Found: C, 62·7; H, 6·5. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·6%). The same dilactone is obtained from the piperidone compound (VI) by hydrolysis with concentrated hydrochloric acid.

The acid product is *cyclopentane-1-acetone-1-acetic acid* (III) (2·05 g.); after crystallising from light petroleum, it melts at 53° (Found: C, 65·0; H, 8·9. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%) and is identical with the synthetic acid described below.

Synthesis of Methyl cyclo*Pentane-1-acetone-1-acetate.*—The an-

hydride (98 g.) of *cyclo*pentane-1 : 1-diacetic acid (Kon and Thorpe, *loc. cit.*, p. 700) is boiled with methyl alcohol (47 c.c.) for 3 hours, the oily methyl hydrogen *cyclo*pentane-1 : 1-diacetate produced (Found for the *silver* salt: Ag, 35·8. $C_{10}H_{15}O_4Ag$ requires Ag, 35·4%) is treated with a slight excess of thionyl chloride, and the crude acid chloride with zinc methyl iodide: from 60 g. of the acid ester, 44 g. of *methyl* cyclo*pentane*-1-*acetone*-1-*acetate* were obtained. The *semicarbazone*, after crystallising from methyl alcohol, melts at 119° (Found: C, 56·5; H, 8·5. $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2%). The ester regenerated from it has b. p. 130°/12 mm., $d_4^{17.7°}$ 1·0386, $n_D^{17.7°}$ 1·46021, whence $[R_L]_D$ = 52·24 (calc., 52·46) (Found: C, 66·5; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%). The ester (7 g.), on being heated with sodium (0·9 g.) in 30 c.c. of alcohol for several hours on the steam-bath, is completely converted into *cyclo*pentane*spirocyclo*hexane-3 : 5-dione, m. p. 136° (Norris and Thorpe, *loc. cit.*, p. 1207). This is the best method of preparing the dione in quantity, and the reduction of this substance to the corresponding hydrocarbon is under investigation in order tc compare this product with that obtained by a different series o reactions.

cyclo*Pentane*-1-*acetone*-1-*acetic Acid* (III).—The methyl este (31 g.) is hydrolysed with potassium hydroxide (30 g.) in aqueous alcoholic solution. The *acid* produced contains some *cyclo*pentane 1 : 1-diacetic acid and is purified in the same way as its *cyclo*hexar analogue; after crystallising from light petroleum, it melts at 5 (Found: C, 65·0; H, 8·8; *M*, by titration, 179. $C_{10}H_{16}O_3$ requir C, 65·2; H, 8·7%; *M*, 184). It is very soluble in most of tl ordinary organic solvents, but insoluble in water. The *sem carbazone*, after crystallising from methyl alcohol, melts at 19 (Found: C, 54·7; H, 8·4. $C_{11}H_{19}O_3N_3$ requires C, 54·7; H, 7·9% The acid, on esterification with methyl alcohol and hydrog chloride, gives the above methyl ester, identified through t semicarbazone, m. p. 119°.

Action of Acetyl Chloride on cyclo*Pentane*-1-*acetone*-1-*acetic Acid* When a mixture of the acid (6 g.) and acetyl chloride (10 c.c. heated on the steam-bath, a vigorous reaction sets in and hydro chloride is given off. Heating is continued for about an hour the unsaturated *lactone* (VIII) is then isolated in the same way the *cyclo*hexane analogue. It is a mobile liquid with a characteri odour. It has b. p. 124°/14 mm., $d_4^{18.9°}$ 1·0573, $n_D^{18.9°}$ 1·49 whence $[R_L]_D$ = 45·42 (calc., 45·17) (Found: C, 71·9; H, $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·4%). When hydrolysed alcoholic potash, it gives the keto-acid, m. p. 53°.

In conclusion, I wish to record my grateful thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in this investigation, and to the Government of Bengal, India, for a foreign scholarship and a grant that has partly defrayed the cost.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, January 17th*, 1929.]

CII.—*Synthesis of Cyclic Compounds. Part V. The Catalytic and the Thermal Decomposition of some Normal Dibasic Acids. A Contribution to the Problem of the Ease of Formation of Simple Carbon Rings.*

By ARTHUR ISRAEL VOGEL.

IT has been shown (J., 1928, 2032) that suberone may be obtained in 40% yield by the dry distillation of a mixture of suberic acid and iron filings in the presence of a small quantity of baryta, although Easterfield and Taylor (J., 1911, **99**, 2299) were unable to obtain satisfactory yields by a similar process. The advantages of this method are: (1) the ketone is prepared directly from the acid without previous preparation of a salt, (2) the distillation is carried out under atmospheric pressure, (3) the ketone is obtained in good yield, and (4) the cost is low (compare the dry distillation of thorium suberate under reduced pressure; Ruzicka and others, *Helv. Chim. Acta*, 1926, **9**, 515). It was clearly desirable not only to investigate the mechanism of the reaction but also to extend it to other normal dibasic acids.

As a result of a series of comparative experiments in which suberic acid was heated with different quantities of iron filings and also baryta, full details of which will be found in the experimental section, it is concluded that an intermediate iron—most probably the ferrous—salt is formed at a relatively low temperature and then undergoes decomposition into the ketone at a somewhat higher temperature. When the quantity of iron present is less than that theoretically required for the formation of a ferrous salt, variable quantities of *n*-heptoic acid are formed; indeed, when no iron is present, *n*-heptoic acid forms the principal product of the reaction (*vide infra*). The use of small quantities of baryta facilitates the formation of the intermediate iron salt, lowers the decomposition temperature, and gives a purer product. Support for the view that an intermediate ferrous salt is formed is provided by the experiments of Easterfield and Taylor (*loc. cit.*), who found that the yields of

stearone obtained by the dry distillation of stearic acid with the equivalent quantity of iron for the formation of the ferrous salt (62%) and of ferrous stearate (60%) at 360° were practically identical.

The yields of ketone obtained from adipic and pimelic acids by the iron method (*i.e.*, the optimum conditions employed for suberic acid) were 51% and 56% respectively. Azelaic acid gave a 10% yield of *cyclo*octanone, and only methyl octyl ketone could be isolated from the distillation of sebacic acid and iron filings (compare Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 389, who isolated 0·5% of suberone, 1·2—1·5% of *cyclo*nonanone, and 0·7% of methyl octyl ketone by the dry distillation of thorium sebacate). The formation and decomposition of the intermediate iron salt of azelaic acid is very much slower than that of suberic acid, so in the dry distillation of a mixture of suberic and azelaic acids under the conditions previously described (Vogel, *loc. cit.*), it is the iron salt of suberic acid which is preferentially formed and decomposed and hence only suberone is obtained. No appreciable quantity of ketone could be isolated from glutaric acid.

A summary of the results is given in Table I; the yields obtained from the calcium and thorium salts (Ruzicka and others, *Helv. Chim. Acta*, 1926, **9**, 505) are appended for purposes of comparison. The last column represents the results obtained by the slow thermal decomposition of the acids (*vide infra*). It is evident from the table

TABLE I.

Salt:	Calcium.	Thorium.	Iron.	Acid.
Glutaric acid	0	0	<1%	0
Adipic "	45%	15%	51	80%
Pimelic "	40—50	70	56	52
Suberic "	35	40	40	<2
Azelaic "	5	20	10	<1
Sebacic "	<1	1·5	<1	<1

that the yields of ketone obtained by the dry distillation of the sal of the dibasic acids cannot be employed as an absolute index ring-forming capacity, as these vary with the metal employe In order, therefore, to obtain experimental evidence for the ease formation of simple carbon rings, some other reaction must employed. Before the method used in the present research described, a critical discussion of the previous work on the subj must be given. The reaction chosen must satisfy at least two co ditions: there must be (1) a main reaction involving the formati of the cyclic compound and (2) an alternative side reaction leadi to an open-chain product. Ingold (J., 1921, **119**, 305) studied action of alkali under standard conditions on α-halogenated

$\alpha\alpha'$-dihalogenated derivatives of dibasic acids, the side reaction being the replacement of the halogen atom by the hydroxyl group, and the progress of ring formation in competition with the side reaction being taken as a measure of the ease of production of the ring. It was shown that, whereas the yield of *cyclo*propane compound was about 50% in the glutaric acid series, only about 1% of *cyclo*butane compound was isolated in the adipic acid series (Ingold, J., 1921, **119**, 951). For pimelic acid, Hassell and Ingold (J., 1926, 1465) state that "the ratio (ring formation) : (hydroxylation) is much greater than in any case previously investigated," but no quantitative figures are given. The reaction, as an index of ring-forming capacity, fails completely for suberic and azelaic acids owing to side reactions (Goss and Ingold, J., 1926, 1471), so that the experimental problem of the relative ease of formation of 5- and 6-membered rings must still be regarded as unsolved.

By assuming the value 115·3° as the angle between the carbon-to-carbon valencies in a polymethylene chain, calculated on the basis of the modified strain theory, and by employing Traube's relative atomic volumes for carbon and hydrogen (Ahren's Vorträge, 1899, 4, 255), Ingold computes the relative ease of formation of some simple carbon rings (Table II, A); the figures thus obtained exhibit

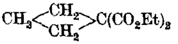
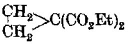
TABLE II.

	3-Ring.	4-Ring.	5-Ring.	6-Ring.	7-Ring.	
Ease of ring formation	0·345	0·427	0·220	0·207	0·730	(A)
Stability	0·927	0·436	0·126	0·084	0·230	(B)
Angle of strain (Baeyer)	24·7°	9·7°	0·7°	−5·3°	−9·5°	(C)
"Heat absorbed" (cals.) (S. and K.) ...	38·1	42·6	16·1	14·3	—	(D)
Energy of C–C link (cals.) (Hückel)	127·2	130·1	136·5	137·5	138·5	(E)
Contribution (cals.) per CH_2	168·5	165·5	159	158	158	(F)

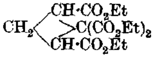
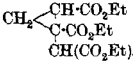
a maximum at *cyclo*butane—in agreement with Ingold's own experimental results—and require the almost equal ease of formation of 5- and 6-membered rings. Ingold seeks to obtain further support for his theoretical calculations by comparing (A) with Stohmann and Kleber's thermal figures (D) (*J. pr. Chem.*, 1892, **45**, 475). This comparison, however, is not justified, since thermal measurements must be compared not with ease of ring formation but with the *stability* of the ring, a quantity (Table II, B) which was also computed by Ingold (*loc. cit.*, p. 309) and exhibits no maximum at *cyclo*butane (compare Hückel, "Fortschritte der Chemie, Physik und Physikalischen Chemie," Bd. 19, Heft 4, 1927, s. 75). Hückel (*Ber.*, 1920, **53**, 1281) states that the correct quantity to be employed for the comparison of the stability of ring systems by means of

thermochemical data is the energy of the C–C linking in the ring (Table II, E) or the contribution in cals. per CH_2 (*ibid.*, p. 11) (Table II, F): these exhibit no maximum at *cyclo*butane.

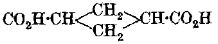
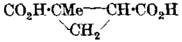
Examples such as (*a*) the greater yield of the *cyclo*butane compound (I) than of the *cyclo*propane compound (II) obtained by the condensation of trimethylene dibromide and ethylene dibromide,

(I.)   (II.)

respectively, with ethyl sodiomalonate (Perkin, J., 1885, **47**, 801; 1887, **51**, 1; Perkin and Prentice, J., 1891, **59**, 823), (*b*) the almost equal yields of *cyclo*butane (III) and *cyclo*propane (IV) compounds obtained in the condensation of ethyl αα′-dibromoglutarate with

(III.)   (IV.)

ethyl sodiomalonate in alcoholic solution (condensation in benzene solution gave a 70—80% yield of III; Ing and Perkin, J., 1925, **127**, 2387), and (*c*) the quantitative production of *cyclo*butane-1 : 3-dicarboxylic acid (V) and not the 3-membered ring compound

(V.)   (VI.)

(VI) by the reduction of αβδ-tribromobutane-βδ-dicarboxylic acid (Perkin and Simonsen, J., 1909, **95**, 1169) are difficult to correlate with Ingold's calculations and point unmistakably to the presence of polar and other factors which render comparison impossible.

Reference must here be made to the important theoretical work of Wojnicz-Sianozencki (*Rocz. Chem.*, 1921, i, 244) on the ease of formation of simple carbon rings. The normal tetrahedral angle, 109° 28′ 24″, in a polymethylene chain (compare Ingold, *loc. cit.*) forms the basis of the calculations and the whole conception is essentially a dynamic one; by applying the theory of probabilities and making certain plausible assumptions relative to the sphere of influence of the carbon atoms, the final result obtained is that

$$\eta_2 > \eta_5 > \eta_6 > \eta_7 > \eta_3 > \eta_4 > \eta_8$$

where η_n represents the probability of formation of an *n*-membered ring, *i.e.*, a double bond is formed more readily than a 5-ring, a 5-ring more readily than a 6-ring, etc. The points of particular interest are: (i) the greater ease of formation of a 3- than a 4-ring a result in agreement with Ingold's calculations, and (ii) the 5-ring should be formed more readily than the 6-ring.

... chosen by the author for the comparison of capacity

of ring formation, which satisfied the two conditions already mentioned and in which polar factors were reduced to a minimum, consisted in the slow thermal distillation of the normal dibasic acids (VII). Decomposition could occur in two ways: the first

$$(CH_2)_n{<}\begin{array}{l}CH_2{\cdot}CO_2H\\ CH_2{\cdot}CO_2H\end{array}\ \text{(VII.)}\quad \begin{array}{l}\nearrow (CH_2)_n{<}\begin{array}{l}CH_2\\ CH_2\end{array}{>}CO + CO_2 + H_2O\ \text{(VIII.)}\\ \searrow (CH_2)_n{<}\begin{array}{l}CH_3\\ CH_2{\cdot}CO_2H\end{array} + CO_2\ \text{(IX.)}\end{array}$$

involves the loss of carbon dioxide and water with the production of the ketone (VIII); the second, the elimination of carbon dioxide only with the formation of a saturated monobasic acid (IX). The reaction products could be easily separated and weighed. Glutaric acid yielded only *n*-butyric acid, but the most interesting results were obtained with adipic and pimelic acids. The yields of *cyclo*pentanone and *cyclo*hexanone were respectively 80% and 52%, thus pointing to the conclusion that the *cyclo*pentane ring is formed more readily than the *cyclo*hexane ring, a result which is not in accord with the theoretical computations of Ingold (Table II, A) but is in agreement with the predictions made by Wojnicz-Sianozencki (*loc. cit.*). Further, the yield of monobasic acid was greater in the pimelic than in the adipic acid series. This observation is not an isolated one, for Perkin (compare *Ber.*, 1902, **35**, 2105) has found that αδ-dibromopentane condenses more readily than αε-dibromopentane with ethyl sodiomalonate with the formation of the corresponding cyclic compounds (X) and (XI), and the 7-membered ring compound (XII) is formed with great difficulty from heptamethylene

$$\text{(X.)}\ \begin{array}{l}CH_2{\cdot}CHMe\\ CH_2{-}CH_2\end{array}{>}C(CO_2Et)_2 \qquad CH_2{<}\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}{>}C(CO_2Et)_2\ \text{(XI.)}$$

$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}CH_2\end{array}{>}C(CO_2Et)_2\ \text{(XII.)}$$

dibromide and ethyl sodiomalonate. Suberic, azelaic, and sebacic acids gave good yields of *n*-heptoic, *n*-octoic, and *n*-nonoic acids and the yields of ketone in the first two cases did not exceed 2%. The yields of *cyclo*pentanone obtained by the dry distillation of adipic acid (80%) and of adipic acid in the presence of 5% of baryta (78%) under comparable conditions are practically identical, so the reaction cannot be regarded as a catalytic one (D.R.-P. 256622; Roger Adams, "Organic Syntheses," 1925, **5**, 37); the effect of the baryta is to lower the decomposition temperature from 313—315° to 288—293° and slightly to accelerate the decomposition.

Aschan (*Annalen*, 1911, **385**, 58; *Ber.*, 1912, **45**, 1603) has described the distillation of adipic, suberic, and sebacic acids in a

current of carbon dioxide, but although he actually isolated only the ketones and monobasic acids, he expressed the view that unsaturated acids also are formed according to the scheme:

$$\begin{array}{l} CH_2\cdot CH_2\cdot CO_2H \\ CH_2\cdot CH_2\cdot CO_2H \end{array} \longrightarrow H_2O + \begin{array}{l} CH_2\cdot CH_2\cdot CO \\ CH_2\cdot CH_2\cdot CO \end{array}\!\!>O \longrightarrow$$

$$CO + \begin{array}{l} CH_2\cdot CH_2\cdot O \\ CH_2\cdot CH_2\cdot CO \end{array} \longrightarrow \begin{array}{l} CH{:}CH_2 \\ CH_2\cdot CH_2\cdot CO_2H \end{array}$$

This view, which was unsupported by experimental evidence, is probably erroneous. Other relevant work is that of Blanc (*Bull. Soc. chim.*, 1908, **3**, 778), who found that the yields of ketones obtained by distillation of the anhydrides of adipic and pimelic acids at 200—220° (a temperature very much lower than that employed in the present research) were about 50%.

The work is being continued and will be extended to other normal and also to substituted acids.

EXPERIMENTAL.

Glutaric Acid.—The following modification of Wislicenus's method (*Annalen*, 1893, **275**, 309) for the preparation of glutaric acid was employed. One part of *cyclo*pentanone was added during 2 hours to 10 parts of boiling dilute nitric acid (2 : 3), and the whole evaporated to dryness on the steam-bath. The residue was extracted twice with benzene–ether, the solvent removed, and the resultant glutaric acid recrystallised first from chloroform and then from benzene–ether. It melted at 97°. Yield: 280 g. of glutaric acid and 90 g. of succinic acid from 400 g. of *cyclo*pentanone (two experiments).

A. Thermal decomposition. The apparatus employed consisted of a 500 c.c. Pyrex distilling flask furnished with a cork carrying a thermometer reaching to within 0·5 cm. of the bottom of the flask and connected to a long water-condenser and receiver. The flask, containing 100 g. of glutaric acid, was placed in a bath, the intervening space packed with copper turnings, and the whole gradually heated, the rate of distillation not exceeding one drop in several seconds. A small quantity of liquid passed over at 290—300° and the temperature then remained constant at 301—304° during the distillation, which lasted 20 hours. There was a carbonaceous residue. The distillate was taken up in ether, the ethereal solutior was washed with excess of dilute aqueous sodium hydroxide anc dried, and the ether evaporated. The neutral fraction (0·4 g.) dic not give a semicarbazone on standing with semicarbazide acetat for some months and was therefore not further investigated. Th [illegible] washings were acidified with dilute sulphuric acid an

steam-distilled; from the steam-distillate, saturated with ammonium sulphate, ether extracted butyric acid, b. p. 160—162°/750 mm., $d_{4^\circ}^{19\cdot9^\circ}$ 0·9595, $n_D^{19\cdot9^\circ}$ 1·3978 (Found for the silver salt: Ag, 55·7. Calc.: Ag, 55·4%).

B. Catalytic decomposition. This term will be applied to the decompositions in which the proportion of iron and baryta was that which gave the highest yield of suberone from suberic acid (Vogel, *loc. cit.*). An intimate mixture of 50 g. of glutaric acid, 50 g. of iron filings, and 2·5 g. of crystallised baryta was slowly distilled exactly as described under (A): these were the standard conditions used throughout the work. There was some frothing at about 270°, some fuming above 290°, and a small distillate passed over at 290—380°. This was taken up in ether, washed with alkali, and recovered (1·5 g.). It distilled at 145—150°/758 mm. (*cyclo*butanone has b. p. 99—101°), and was not further investigated since it gave only a sticky semicarbazone.

Adipic Acid.—The adipic acid was obtained from the Deutsches Hydrierungs Akt. and had m. p. 152°.

A. Thermal decomposition. 200 G. were distilled during 12 hours from a litre Pyrex distilling flask; the major portion passed over at 313—315°, but the temperature rose to 320° towards the end of the distillation. The distillate was treated with excess of dilute ammonia solution, the ammoniacal layer separated, and the residual liquid dried with calcium chloride and distilled. 92 G. of *cyclo*pentanone, b. p. 131—132°, were obtained and there was hardly any residue of high boiling point. The excess of ammonia was evaporated from the ammoniacal washings, and from the neutral solution silver salts were precipitated (12·4 g. Found: Ag, 54·4%). These were decomposed with dilute sulphuric acid, and *n*-valeric acid, containing a little adipic acid in suspension, was obtained; it boiled at 183—185°/770 mm. (Found for the silver salt: Ag, 51·9. Calc.: Ag, 51·7%). The yield of ketone (80%) was unaffected if the distillation was carried out in lots of 50 g. from a 500 c.c. Pyrex distilling flask; the duration of the distillation was then 6 hours.

B. Decomposition in the presence of an equivalent quantity of iron. When 200 g. of adipic acid and 77 g. of iron filings were slowly heated, the temperature rose fairly rapidly to 250°, the ketone passed over mainly above 290°, and the temperature rose to 360° towards the end of the distillation. The yield of *cyclo*pentanone was 70 g. or 61%.

C. Decomposition in the presence of 5% by weight of baryta. 200 G., mixed with 10 g. of crystallised baryta, were similarly heated. The distillate passed over at 288—293°/769 mm. and was worked up as

scribed under (A). The yield of *cyclo*pentanone was 90 g. or 3%.

D. Catalytic decomposition. When a mixture of 200 g. of adipic cid, 200 g. of iron filings, and 10 g. of baryta was heated, after ater had passed over, the ketone began to distil at 260° and most assed over at 290—300°; the temperature was finally raised to 60°. The yield of *cyclo*pentanone was 59 g. or 51%; there was 0 g. of a product of high boiling point (compare the distillation of alcium adipate; Wislicenus, *Annalen*, 1893, **275**, 309; Wallach, *Ber.*, 1896, **29**, 2955) which probably contained some *cyclo*pentyldene*cyclo*pentanone.

Pimelic Acid.—This was prepared in fair yield by the condensation of αγ-dibromopropane and ethyl sodiomalonate (Perkin and Prentice, J., 1887, **51**, 20; 1891, **59**, 823) and hydrolysis of the resultant ethyl pentanetetracarboxylate with 50% sulphuric acid; a somewhat better yield was obtained by employing 4 mols. of ethyl sodiomalonate per mol. of αγ-dibromopropane (compare Baeyer, *Annalen*, 1894, **278**, 100). The most convenient method was the following one: αε-dibromopentane, b. p. 112—113°/22 mm. (Dox and Yoder, *J. Amer. Chem. Soc.*, 1921, **43**, 1366: it may now be prepared in good yield from ethyl glutarate; Müller and Rölz, *Monatsh.*, 1928, **50**, 105) was converted, by refluxing it with 2 mols. of alcoholic potassium cyanide, into the dinitrile, b. p. 164—165°/13 mm. (von Braun, *Ber.*, 1904, **37**, 3588, gives b. p. 171—172°/12 mm.; Hamonet, *Compt. rend.*, 1904, **139**, 59, gives b. p. 175—176°/14 mm.), and the latter hydrolysed by heating under reflux for 9 hours with 12—15 times its weight of 50% sulphuric acid; the pimelic acid separated as a crystalline solid from the cooled solution (yield, almost quantitative). The method of von Braun and of Hamonet (*loc. cit.*), involving the use of a sealed tube, is less convenient and is difficult to carry out with large quantities of material. On recrystallisation from benzene containing 5% of ether, the pimelic acid separated in prisms, m. p. 105—106°.

A. Thermal decomposition. 50 G. were distilled during 6 hours exactly as described under adipic acid (A). The distillate, which passed over mostly at 334—336°, was mixed with pure ether and treated with an excess of dilute aqueous ammonia, the ethereal solution dried, and the ether slowly removed through a long column The residual liquid had b. p. 155°/758 mm., $d_4^{15.7°}$ 0·9489, $n_D^{15.4°}$ 1·452[illegible] (Vogel, J., 1928, 2030, gives for *cyclo*hexanone regenerated from th bisulphite compound, $d_4^{15.7°}$ 0·9492, $n_D^{16.0°}$ 1·4521) and gave a quanti tative yield of *cyclo*hexanonesemicarbazone, m. p. 166° (yield 16·0 g. or 52%). From the ammoniacal washings, silver *n*-hexoat [illegible] (Found: Ag, 48·9. Calc.: Ag, 48·5%) was obtained.

B. Catalytic decomposition. When 50 g. were heated during 6 hours, a pale yellow liquid distilled at 318—360° which gave 17·1 g. of *cyclo*hexanone (yield, 56%) and 4·0 g. of a high-boiling product which was not investigated.

Suberic Acid.—This was prepared from castor oil (Baker and Ingold, J., 1923, **123**, 122; Vogel, J., 1928, 2032) and melted at 140°.

A. Thermal decomposition. 50 G. were distilled during 5 hours. The distillate, which passed over at 341—348°, was separated by means of ether and dilute sodium hydroxide solution into a neutral fraction (0·9 g.), which gave suberonesemicarbazone, and an acid fraction; the latter, after purification by steam distillation and treatment with ether, gave 15·5 g. of *n*-heptoic acid, b. p. 120°/18 mm., $d_{4°}^{18·8°}$ 0·9212, $n_D^{18·8°}$ 1·4255 (Found for the silver salt: Ag, 45·7. Calc.: Ag, 45·6%).

B. Decomposition in the presence of 5% by weight of baryta. 50 G., mixed with 2·5 g. of crystallised baryta, were slowly distilled. A liquid passed over at 336—342° (mainly at 336—337°) and after being worked up as described under (A), gave a small quantity of suberonesemicarbazone (yield, $\not>$2%) and 12·9 g. of *n*-heptoic acid, b. p. 121°/18 mm., $d_{4°}^{17·1°}$ 0·9231, $n_D^{17·1°}$ 1·4265.

C. Decomposition in the presence of 5% by weight of iron filings. This is the original "catalytic" process described in D.R.-P. 256622, for which an excellent yield of suberone is claimed. When 50 g. of suberic acid, mixed with 2·5 g. of iron filings, were distilled, a liquid passed over at 308—326°. The temperature was raised above 360° after 5 hours; considerable frothing and fuming set in and a further small quantity of liquid distilled over. The distillate was treated in the usual way. The neutral fraction yielded 2·5 g. of a liquid, b. p. 178—186°/769 mm., on distillation; treatment with semicarbazide acetate furnished an opaque granular semicarbazone, obviously impure, which after five crystallisations from dilute methyl alcohol melted at 162—163° and was identical with suberonesemicarbazone. The acid fraction gave 8·5 g. of *n*-heptoic acid, b. p. 121°/19 mm.

D. Decomposition in the presence of one-half the equivalent weight of iron filings. 50 G., mixed with 8·2 g. of iron filings (half the quantity required for the formation of a ferrous salt), were distilled during 6 hours. There was a small amount of frothing at first and a substance with a pungent acid odour passed over at 316—328°; when about half the total distillate has passed over, the odour of the distillate changed to a ketonic one, this process being accompanied by frothing and fuming in the flask. The temperature was raised towards the end of the decomposition until no further distillate was obtained. The distillate was worked up as detailed under (C) and

yielded 1·8 g. of *n*-heptoic acid and 7·7 g. of a ketonic fraction, b. p. 178—188°/766 mm., $d_{4°}^{19·9°}$ 0·9242, $n_D^{19·9°}$ 1·4584, which afforded suberonesemicarbazone, m. p. 162—163°, after three crystallisations from dilute methyl alcohol.

E. Decomposition in the presence of an equivalent quantity of iron filings. 50 G., mixed with 16·5 g. of iron filings, were slowly distilled. There was considerable frothing and fuming at first, and some water distilled, followed by a colourless liquid of ketonic odour at 296—312° (chiefly at 296—298°); when the temperature was finally raised to about 400°, a small quantity of a blue liquid passed over. The distillate was mixed with ether, washed with dilute alkali solution and dried, and the ether removed; the residual liquid yielded on fractionation (1) a practically colourless liquid (8·0 g.), b. p. 177—185°/756 mm., chiefly at 179—180°/756 mm., $d_{4°}^{19·5°}$ 0·9259, $n_D^{19·5°}$ 1·4580, which gave suberonesemicarbazone, m. p. 162°, after three crystallisations from dilute methyl alcohol, (2) a pale blue liquid (3·2 g.), b. p. 186—205°/756 mm., which became yellowish-brown on standing and contained some suberone, and (3) a dark-coloured liquid (3·0 g.), b. p. above 205°/756 mm., which was not investigated. The alkaline washings gave 0·1 g. of *n*-heptoic acid.

F. Decomposition in the presence of an equal weight of iron filings. 50 G., mixed with 50 g. of iron filings, were slowly distilled. There was a considerable amount of fuming and frothing while the temperature was 280—330°; the fuming then subsided, and a pale yellow liquid of ketonic odour passed over at 340—370°. The temperature was raised until no further distillate was obtained; the last fraction was bluish-green. After being worked up as detailed under (C), the distillate yielded 10·0 g. of a liquid, b. p. 180—182°/766 mm., $d_{4°}^{19·4°}$ 0·9326, $n_D^{19·4°}$ 1·4582, which furnished suberonesemicarbazone, m. p. 162—163° after one crystallisation from dilute methyl alcohol; there was also a dark-coloured residue (0·9 g.).

The decomposition of suberic acid in the presence of an equal weight of iron filings and 5% by weight of baryta has previously been described (J., 1928, 2035), and that experiment and experiments C, D, E, and F indicate clearly that increasing the proportion of iron increases the purity of the resultant suberone, as evidenced by the boiling point, density, refractivity, and semicarbazone formation.

Azelaic Acid.—This was prepared by the oxidation of ricinoleic acid with potassium permanganate (Maquenne, *Bull. Soc. chim.* 1899, 21, 1061) and after recrystallisation from benzene melted 106—107°.

A. Thermal decomposition. 50 G. were distilled during 8 hours

The distillate, which passed over at 354—357°, was worked up as described under suberic acid (A). The neutral product gave the following fractions on distillation: (i) b. p. 85—155°, *ca.* 1 g., (ii) b. p. 180—230°, 1·4 g. Treatment of the latter with semicarbazide acetate yielded, after long standing, a semicarbazone the m. p. of which could not be raised above 105—110° after several crystallisations from dilute methyl alcohol; it was not further investigated owing to he small quantity available, but was clearly impure *cyclo*octanonesemicarbazone. The alkaline washings gave 5·0 g. of *n*-octoic acid, b. p. 129—130°/16 mm. (Found for the silver salt: Ag, 43·4. Calc.: Ag, 43·1%).

B. Catalytic decomposition. 80 G., mixed with 80 g. of iron filings and 4 g. of crystallised baryta, were slowly distilled. (The intermediate iron salt is only slowly formed and unless the following experimental conditions are maintained a very poor yield of ketone is obtained.) The temperature was slowly raised to 250°, kept at 250—300° for at least 2 hours, and then slowly raised. Some frothing and fuming occurred at 370—380° and a liquid with a ketonic odour distilled; the distillation was conducted very slowly at 370—390° during 20 hours until the liquid ceased to distil. The total duration of the distillation was 27 hours. The distillate gave by the usual treatment a neutral fraction, which was distilled under diminished pressure, the following fractions being collected: (i) up to 67°/17 mm., 3·7 g.; (ii) b. p. 67—74°/17 mm., 1·9 g.; (iii) 74—86°, chiefly 77—81°/17 mm., 2·8 g.; (iv) 86—130°/17 mm., 5·4 g. Each fraction was treated with semicarbazide acetate; fraction (iii) yielded a semicarbazone immediately, but fractions (i) and (ii) only after some time. The semicarbazone from fraction (iii) after recrystallisation from dilute methyl alcohol was caseous and melted at 95—120°; further recrystallisation from dilute methyl alcohol, followed by trituration with light petroleum (b. p. 60—80°) and recrystallisation from benzene and from dilute methyl alcohol, gave lustrous feathery plates, m. p. 166—167°, of *cyclo*octanonesemicarbazone (Found: C, 58·7; H, 9·3. Calc.: C, 59·0; H, 9·4%). The melting point of a mixture with an authentic specimen kindly supplied by Professor L. Ruzicka was 166—167·5°. The m. p.'s of mixtures with *cyclo*hexanonesemicarbazone (m. p. 166°) and with suberonesemicarbazone (m. p. 162—163°) were respectively 139—149° and 149—156°. The semicarbazone derived from fraction (ii) behaved similarly, but was less pure. A poor yield of semicarbazone was obtained from fraction (i). The yield of *cyclo*octanone was about 10%.

C. Catalytic decomposition of "azelaic acid" isolated from "mixed acids" (compare J., 1928, 2035). The acid was isolated from the

yielded 1·8 g. of *n*-heptoic acid and 7·7 g. of a ketonic fraction, b. p. 178—188°/766 mm., $d_4^{19.9°}$ 0·9242, $n_D^{19.9°}$ 1·4584, which afforded suberonesemicarbazone, m. p. 162—163°, after three crystallisations from dilute methyl alcohol.

E. Decomposition in the presence of an equivalent quantity of iron filings. 50 G., mixed with 16·5 g. of iron filings, were slowly distilled. There was considerable frothing and fuming at first, and some water distilled, followed by a colourless liquid of ketonic odour at 296—312° (chiefly at 296—298°); when the temperature was finally raised to about 400°, a small quantity of a blue liquid passed over. The distillate was mixed with ether, washed with dilute alkali solution and dried, and the ether removed; the residual liquid yielded on fractionation (1) a practically colourless liquid (8·0 g.), b. p. 177—185°/756 mm., chiefly at 179—180°/756 mm., $d_4^{19.5°}$ 0·9259, $n_D^{19.5°}$ 1·4580, which gave suberonesemicarbazone, m. p. 162°, after three crystallisations from dilute methyl alcohol, (2) a pale blue liquid (3·2 g.), b. p. 186—205°/756 mm., which became yellowish-brown on standing and contained some suberone, and (3) a dark-coloured liquid (3·0 g.), b. p. above 205°/756 mm., which was not investigated. The alkaline washings gave 0·1 g. of *n*-heptoic acid.

F. Decomposition in the presence of an equal weight of iron filings. 50 G., mixed with 50 g. of iron filings, were slowly distilled. There was a considerable amount of fuming and frothing while the temperature was 280—330°; the fuming then subsided, and a pale yellow liquid of ketonic odour passed over at 340—370°. The temperature was raised until no further distillate was obtained; the last fraction was bluish-green. After being worked up as detailed under (C), the distillate yielded 10·0 g. of a liquid, b. p. 180—182°/766 mm., $d_4^{19.4°}$ 0·9326, $n_D^{19.4°}$ 1·4582, which furnished suberonesemicarbazone, m. p. 162—163° after one crystallisation from dilute methyl alcohol; there was also a dark-coloured residue (0·9 g.).

The decomposition of suberic acid in the presence of an equal weight of iron filings and 5% by weight of baryta has previously been described (J., 1928, 2035), and that experiment and experiments C, D, E, and F indicate clearly that increasing the proportion of iron increases the purity of the resultant suberone, as evidenced by the boiling point, density, refractivity, and semicarbazone formation.

Azelaic Acid.—This was prepared by the oxidation of ricinoleic acid with potassium permanganate (Maquenne, *Bull. Soc. chim.* 1899, 21, 1061) and after recrystallisation from benzene melted at 106—107°.

A. Thermal decomposition. 50 G. were distilled during 8 hour

The distillate, which passed over at 354—357°, was worked up as described under suberic acid (A). The neutral product gave the following fractions on distillation : (i) b. p. 85—155°, *ca.* 1 g., (ii) b. p. 180—230°, 1·4 g. Treatment of the latter with semicarbazide acetate yielded, after long standing, a semicarbazone the m. p. of which could not be raised above 105—110° after several crystallisations from dilute methyl alcohol; it was not further investigated owing to the small quantity available, but was clearly impure *cyclo*octanonesemicarbazone. The alkaline washings gave 5·0 g. of *n*-octoic acid, b. p. 129—130°/16 mm. (Found for the silver salt : Ag, 43·4. Calc. : Ag, 43·1%).

B. Catalytic decomposition. 80 G., mixed with 80 g. of iron filings and 4 g. of crystallised baryta, were slowly distilled. (The intermediate iron salt is only slowly formed and unless the following experimental conditions are maintained a very poor yield of ketone is obtained.) The temperature was slowly raised to 250°, kept at 250—300° for at least 2 hours, and then slowly raised. Some frothing and fuming occurred at 370—380° and a liquid with a ketonic odour distilled; the distillation was conducted very slowly at 370—390° during 20 hours until the liquid ceased to distil. The total duration of the distillation was 27 hours. The distillate gave by the usual treatment a neutral fraction, which was distilled under diminished pressure, the following fractions being collected : (i) up to 67°/17 mm., 3·7 g.; (ii) b. p. 67—74°/17 mm., 1·9 g.; (iii) 74—86°, chiefly 77—81°/17 mm., 2·8 g.; (iv) 86—130°/17 mm., 5·4 g. Each fraction was treated with semicarbazide acetate; fraction (iii) yielded a semicarbazone immediately, but fractions (i) and (ii) only after some time. The semicarbazone from fraction (iii) after recrystallisation from dilute methyl alcohol was caseous and melted at 95—120°; further recrystallisation from dilute methyl alcohol, followed by trituration with light petroleum (b. p. 60—80°) and recrystallisation from benzene and from dilute methyl alcohol, gave lustrous feathery plates, m. p. 166—167°, of *cyclo*octanonesemicarbazone (Found : C, 58·7; H, 9·3. Calc. : C, 59·0; H, 9·4%). The melting point of a mixture with an authentic specimen kindly supplied by Professor L. Ruzicka was 166—167·5°. The m. p.'s of mixtures with *cyclo*hexanonesemicarbazone (m. p. 166°) and with suberonesemicarbazone (m. p. 162—163°) were respectively 139—149° and 149—156°. The semicarbazone derived from fraction (ii) behaved similarly, but was less pure. A poor yield of semicarbazone was obtained from fraction (i). The yield of *cyclo*octanone was about 10%.

C. Catalytic decomposition of " azelaic acid " isolated from " mixed acids " (compare J., 1928, 2035). The acid was isolated from the

mother-liquor of the suberic acid preparation and melted at 105—106° after several crystallisations from benzene. An intimate mixture of 100 g. of the acid, 100 g. of iron filings, and 5 g. of crystallised baryta was slowly distilled from a 2-litre Pyrex distilling flask. Considerable frothing and fuming took place at 200—260°, the distillate passed over chiefly at 325—340°, and the distillation was stopped at 360°. The product was worked up exactly as described under B and gave the following fractions on distillation: (i) b. p. 62—70°/13 mm., $d_4^{17·7°}$ 0·9133, $n_D^{17·7°}$ 1·4571, 6·7 g., (ii) b. p. 70—80°/13 mm., $d_4^{17·7°}$ 0·9293, $n_D^{17·7°}$ 1·4611, 3·1 g., (iii) b. p. 80—130°/13 mm., 2 g. Fractions (i) and (ii) yielded only suberonesemicarbazone on treatment with semicarbazide acetate. A minute quantity of the *cyclo*octanone fraction was isolated by Ruzicka and Brugger's sodium bisulphite method. Suberone is therefore the main product.

Sebacic Acid.—Boot's pure sebacic acid, m. p. 130°, was employed.

A. Thermal decomposition. 50 G. were distilled during 8 hours. The distillate, which passed over at 359—364°, was separated into a neutral fraction (0·9 g.), which gave a poor yield of a sticky semicarbazone on long standing with semicarbazide acetate, and an acid fraction consisting of *n*-nonoic acid (7·0 g.), b. p. 142—143°/16 mm., $d_4^{19·0°}$ 0·9096, $n_D^{19·0°}$ 1·4343 (Found for the silver salt: Ag, 41·1. Calc.: Ag, 40·8%).

B. Catalytic decomposition. 75 G. of sebacic acid, mixed with 75 g. of iron filings and 3·5 g. of crystallised baryta, were slowly distilled until nothing further passed over. The distillate (yield relatively small) gave a neutral fraction which was separated by distillation under reduced pressure into (i) 3·5 g., b. p. 46°/15 mm.–80°/12 mm., (ii) 1·7 g., b. p. 80—92°/12 mm., (iii) 1·3 g., b. p. 92–100°/12 mm., (iv) a blue liquid (2·2 g.), b. p. 100—120°/12 mm. A[illegible] the fractions were treated separately with semicarbazide acetate a crystalline semicarbazone was obtained immediately and i[illegible] excellent yield from fraction (iii), but only slowly from fractions ([illegible] and (ii). The semicarbazone from (iii) after three crystallisatio[illegible] from dilute methyl alcohol melted at 122—123°, the m. p. bei[illegible] unaffected by further crystallisation from the same or other solvent it was clearly methyl octyl ketone semicarbazone (Found: C, 61·[illegible] H, 10·8. Calc.: C, 62·0; H, 10·9%) (Ruzicka and Brugg[illegible] *Helv. Chim. Acta*, 1926, **9**, 397, give m. p. 120°; Pickard and Kenyo[illegible] J., 1911, **99**, 57, give m. p. 121°). The semicarbazones from fractio[illegible] (i) and (ii) melted at 116° after three crystallisations from dil[illegible] methyl alcohol and were shown by mixed m. p. determinations a[illegible] analyses to be identical with the semicarbazone from fraction (i[illegible] No other semicarbazone was isolated.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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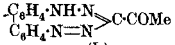
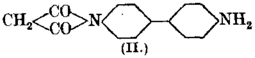
CIII.—*Corrections in the Chemistry of Diphenyl Derivatives of the "Kaufler" Type, and the Formation of Dibenzoctdiazines.*

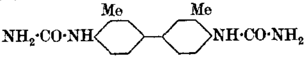
By RAYMOND JAMES WOOD LE FÈVRE.

THE reinvestigation of compounds of the type cited by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250), begun by Le Fèvre and Turner (J., 1926, 2476) for such as were derivatives of benzidine, was extended by Kuhn, Jacob, and Furter (*Annalen*, 1927, **455**, 254) to include those derived from *NN'*-dialkylbenzidines, 4 : 4'-diaminodiphenylmethane, and diaminonaphthalene. There remained unexamined, however, the "malonylbenzidine" of Remfry (J., 1911, **99**, 610), "thiocarbonyl- and carbonyl-dianisidines" (Starke, *J. pr. Chem.*, 1899, **59**, 216), "carbonyl-*o*-tolidine" aud "oxalyl-*o*-tolidine" (Taussig, *Monatsh.*, 1904, **25**, 375), and "*cyclo*formazyl methyl ketone" (formulated as I by Wedekind, *Annalen*, 1898, **300**, 251).

The first three of these substances react with salicylaldehyde to give, in each case, a *salicylidene* derivative (compare Le Fèvre and Turner, *loc. cit.*), indicating the presence of a free amino-group (or groups). Remfry's compound is probably (II), since it forms a *sulphate* and its salicylidene derivative is a well-defined crystalline substance (compare salicylidenemonophthalylbenzidine, Le Fèvre and Turner, *loc. cit.*).

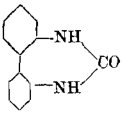

(I.)

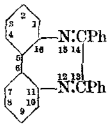

(II.)


(III.)

"Carbonyl-*o*-tolidine" is evidently (III), since (1) it is formed in best yield by heating 1 mol. of *o*-tolidine with 2 mols. of carbamide and (2) it can be obtained by mixing solutions of *o*-tolidine hydrochloride and potassium cyanate. Taussig's "oxalylbenzidine" does not react with salicylaldehyde, and analysis shows it to be the 4 : 4'-*di*-

ethyloxamido-3 : 3′-*dimethyldiphenyl* to be expected from the interaction of ethyl oxalate with *o*-tolidine, which should resemble that of ethyl oxalate with benzidine (Le Fèvre and Turner, J., 1928, 245). Wedekind's directions for the preparation of "*cyclo*formazyl methyl ketone" have been carried out on several occasions, but the products were always coloured inseparable mixtures apparently containing phenolic impurities.

(IV.) 



(V.)

The condensation products of 2 : 2′-diaminodiphenyl with carbamide and with benzil (Niementowski, *Ber.*, 1901, **34**, 3330) are evidently *NN*′-carbonyl-2 : 2′-diaminodiphenyl (IV) and 13 : 14-diphenyldibenzoct-12 : 15-diazine (V), respectively, since, like 13 : 14-(*oo*′-*diphenylylene*)*dibenzoct*-12 : 15-*diazine* and 3 : 8-*dibromo*-13 : 14-(*oo*′-*diphenylylene*)*dibenzoct*-12 : 15-*diazine*, they are inert towards boiling salicylaldehyde, do not form sulphates, and, in addition, are obtained in maximum yields when the reactants are taken in molecular proportion. *NN*′-*Thiocarbonyl*-2 : 2′-*diaminodiphenyl* was readily formed by the interaction of carbon disulphide with 2 : 2′-diaminodiphenyl.

Although the formation of seven-membered rings between the 2- and the 2′-position of diphenyl is well known [*e.g.*, diphenic anhydride from diphenic acid or from fluorenone-4-carboxylic acid (Underwood and Kochmann, *J. Amer. Chem. Soc.*, 1923, **45**, 3073), and diphenimide from phenanthraquinonemonoxime (Wegerhof, *Ber.*, 1888, **21**, 2356; *Annalen*, 1889, **252**, 16, 25)], cases of the facile formation of eight-membered rings between these positions are rare (compare Kenner and Stubbings, J., 1921, **119**, 593; Barber and Smiles, J., 1928, 1141): presumably the rings so obtained are strainless, possibly in consequence of the diphenyl nuclei having revolved about their common axis (as in IV) to give structures having a rigidity greater than that of the *d*- and *l*-forms of the uniaxial non-coplanar diphenic acids (see *Ann. Reports*, 1927).

2 : 2′-Diacetamidodiphenyl was readily dibrominated, giving 5 : 5′-*dibromo*-2 : 2′-*diacetamidodiphenyl*. The corresponding *amine* and phenanthraquinone slowly formed a diphenylylenedibenzoctdiazine in contrast with 4 : 4′-*dibromo*-2 : 2′-*diaminodiphenyl*, which remained unaffected under the same treatment. No definite compounds were isolated from the interaction of 2 : 2′-diaminodi-

phenyl with ethyl malonate, ethyl phthalate, or ethyl oxalate (compare Le Fèvre and Turner, J., 1928, 245).

The ability of the aromatic nuclei in 2 : 2′-diaminodiphenyl to rotate about their common axis is further indicated by the complete absence of steric hindrance during *NN′*-disubstitution : *e.g.*, with the appropriate reagents, *disalicylidene*, dibenzoyl, diacetyl, and diformyl (Täuber, *Ber.*, 1891, **24**, 198) derivatives are formed *exclusively*. Similarly, 1-chloro-2 : 4-dinitrobenzene condenses with 2 : 2′-diaminodiphenyl to give mainly 2 : 2′-*di*(2″ : 4″-*dinitrophenylamino*)*diphenyl*, accompanied by some N-2′ : 4′-*dinitrophenylcarbazole*. The ready formation of α- and β-*naphthyl* and *benzyl hydrogen diphenates* from diphenic anhydride and the corresponding hydroxylic compounds further illustrates essentially the same point.

EXPERIMENTAL.

4-*Salicylideneamino*-4′-*malonylamidodiphenyl*.—A solution of " malonylbenzidine " (prepared according to Remfry, *loc. cit.*) in cold sulphuric acid gave on dilution with ice a colourless amorphous *sulphate* [Found : N, 9·5. $(C_{15}H_{12}O_2N_2)_2,H_2SO_4$ requires N, 9·3%]. A few grams of the base were boiled with an excess of a salicylaldehyde–phenol mixture and the yellowish-red solution produced was cooled. The *salicylidene* derivative crystallised from phenol in light yellow, thin plates, m.p. 298—300° (Found : N, 8·0. $C_{22}H_{16}O_3N_2$ requires N, 7·9%).

Action of Salicylaldehyde on Carbonyl- and Thiocarbonyl-dianisidines.—These substances (prepared essentially as described by Starke, *loc. cit.*), on subjection to the above treatment, slowly formed yellow insoluble powders, which were repeatedly extracted with boiling alcohol [Found : N, from 7·6 to 7·8% for the carbonyl derivative and from 7·2 to 7·5% for the thiocarbonyl derivative. $C_{22}H_{18}O_4N_2$ and $C_{22}H_{18}O_3N_2S$ require N, 7·5 and 7·2%, respectively. The more probable formulæ $(C_{21}H_{18}O_3N)\cdot NH\cdot CO\cdot NH(C_{21}H_{18}O_3N)$ and $(C_{21}H_{18}O_3N)\cdot NH\cdot CS\cdot NH(C_{21}H_{18}O_3N)$ require N, 7·8 and 7·6%, respectively].

" Oxalyl-*o*-tolidine " (Taussig, *loc. cit.*), after dissolution in boiling salicylaldehyde and precipitation by alcohol, gave a colourless powder, m. p. above 300° (Found : N, 6·9. $C_{22}H_{24}O_6N_2$ requires N, 6·8%).

Preparation of 2 : 2′-*Diaminodiphenyl*.—The addition of sand in the preparation of 2 : 2′-dinitrodiphenyl (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2177) is unnecessary. To 60 g. of gently boiling *o*-chloronitrobenzene, 60 g. of copper bronze were slowly added, and the mixture was heated under a long (2 m.) air-condenser over a small flame ; reaction was complete after ½ hour. The product was thrice

extracted with rectified spirit (50 c.c.) and purified in the usual manner. It was reduced with iron, water, and hydrochloric acid to 2 : 2′-*diaminodiphenyl* (yield, 50—60%), which was extracted from the iron paste by boiling alcohol and precipitated as sulphate.

2 : 2′-*Disalicylideneaminodiphenyl* formed long yellow needles, m. p. 153—154° (Found : N, 7·3. $C_{26}H_{20}O_2N_2$ requires N, 7·2%). The same product was formed when half the calculated weight of salicylaldehyde was used.

NN′-*Thiocarbonyl*-2 : 2′-*diaminodiphenyl*.—A mixture of diaminodiphenyl (2 g.), carbon disulphide (10 c.c.), and ethyl alcohol (50 c.c.) was boiled under reflux for 1 day. On cooling over-night, bunches of colourless needles separated, m. p. 242—243°. Recrystallisation from salicylaldehyde gave colourless flakes, m. p. 243° (Found : N, 12·5. $C_{13}H_{10}N_2S$ requires N, 12·4%).

13 : 14-(oo′-*Diphenylylene*)*dibenzoct*-12 : 15-*diazine*.—Solutions of 7·4 g. of 2 : 2′-diaminodiphenyl in 40 c.c. of hot acetic acid and of 8·3 g. of phenanthraquinone in 160 c.c. were mixed and kept at 100° for 2 hours. After 12 hours, a canary-yellow, crystalline powder (11 g.) was filtered off and recrystallised from much boiling acetic acid, the *octdiazine* being obtained in small compact crystals, m. p. 268—269° (Found : N, 8·0. $C_{26}H_{16}N_2$ requires N, 7·9%).

Repetition of the preparation of Täuber's "di-*m*-nitrodi-*o*-aminobiphenyl" (*Ber*., 1892, **25**, 129) has always given a product which is probably a mixture of (chiefly) the 5 : 5′-, 4 : 4′, and 4 : 5′-dinitro-derivatives, together with the 3 : 3′- and 3 : 5′-compounds. Attempts to prepare dinitro-octdiazines from it were unsuccessful, as was also the condensation of 2 : 2′-diaminodiphenyl and benzil-3 : 3′-disulphonic acid (Kafka, *Ber*., 1891, **24**, 794).

5 : 5′-*Dibromo*-2 : 2′-*diacetamidodiphenyl*.—A solution of 7 g. of 2 : 2′-diacetamidodiphenyl (prepared by Brady and McHugh's process, J., 1923, **123**, 2047, for diacetylbenzidine) in 50 c.c. of acetic acid was mixed with 9 g. of bromine in 30 c.c. of acetic acid and heated at 90—100° for 15 minutes. The *dibromo*-derivative (5 g.) obtained crystallised from slightly diluted acetic acid as a heavy colourless, granular powder, m. p. 266—267° (Found : N, 6·[illegible] $C_{16}H_{14}O_2N_2Br_2$ requires N, 6·5%). A further 5·8 g. were obtained from the bromination mother-liquor (total yield, about 90%).

5 : 5′-*Dibromo*-2 : 2′-*diaminodiphenyl*, prepared by refluxing the diacetyl derivative (2 g.) with 40 c.c. of 2*N*-sodium hydroxide and 30 c.c. of alcohol for 10 hours, separated on cooling and crystallised from rectified spirit in colourless needles, m. p. 140—141° (Found : N, 8·2. $C_{12}H_{10}N_2Br_2$ requires N, 8·2%).

5 : 5′-*Dibromo*-2 : 2′-*disalicylideneaminodiphenyl* formed a yellow [illegible] powder, sparingly soluble in the common solvent

m. p. 263—265° (Found: N, 5·2. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%).

3 : 8-*Dibromo*-13 : 14-(oo'-*diphenylylene*)*dibenzoct*-12 : 15-*diazine*. —A mixture of 3·4 g. of 5 : 5'-dibromo-2 : 2'-diaminodiphenyl and 2·1 g. of phenanthraquinone was heated at 100° with 150 c.c. of acetic acid for 8 hours. The *octdiazine* obtained on cooling was sparingly soluble in the ordinary solvents but crystallised from phenol–acetic acid in small, yellow, granular crystals, m. p. above 280° (Found: N, 5·6. $C_{26}H_{14}N_2Br_2$ requires N, 5·4%).

Reduction of 4 : 4'-*Dibromo*-2 : 2'-*dinitrodiphenyl*.—A mixture of 10 g. of iron filings (previously boiled with dilute hydrochloric acid), 30 c.c. of water, and 2 g. of the dibromo-compound (prepared according to Ullmann and Bielecki, *loc. cit.*, from 2 : 5-dibromo-1-nitrobenzene) was heated at 100° for 6 hours and frequently stirred. The iron residues were separated from the diluted mixture and extracted witb alcohol. A portion of the extract, after being boiled with salicylaldehyde, gave a *disalicylidene* derivative, m. p. 210—211° (Found: N, 5·2. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%); the remainder, when evaporated to the crystallisation point and cooled, gave the diamine as a colourless powder, m. p. 192—194°.

Interaction of 2 : 2'-*Diaminodiphenyl with* 1-*Chloro*-2 : 4-*dinitrobenzene*.—5 G. of the diamine and 15 g. of chlorodinitrobenzene were gently boiled together for 10 minutes, hydrogen chloride being evolved. The dark red reaction mixture was extracted with four lots (20 c.c.) of boiling alcohol. The extracts, on cooling, deposited light yellow plates, m. p. 163°, which crystallised from alcohol–salicylaldehyde in long yellow needles, m. p. 177—178°, of 2 : 2'-*di*-(2'' : 4''-*dinitrophenylamino*)*diphenyl* (Found: N, 16·7. $C_{24}H_{16}O_8N_6$ requires N, 16·3%). The residue from the alcoholic extraction crystallised from acetic acid in red plates, m. p. 216—217°, of N-2' : 4'-*dinitrophenylcarbazole* (Found: N, 12·7. $C_{18}H_{11}O_4N_3$ requires N, 12·6%).

Benzyl Hydrogen Diphenate.—Benzyl alcohol (10 g.) was heated at 160° for 2 hours with 20 g. of diphenic anhydride, the product dissolved in toluene, and the solution extracted with aqueous sodium carbonate. Acidification of the extract gave a gum, which was dried in benzene solution with sodium sulphate and recovered by evaporation; it solidified when cooled and scratched. The solid was sparingly soluble in the lighter petroleums and very soluble in benzene and alcohol but crystallised from 50% water–acetic acid in cubes, m. p. 112—113° (Found: C, 75·7; H, 4·9. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%).

α-*Naphthyl Hydrogen Diphenate*.—A mixture of α-naphthol (4·3 g.) and diphenic anhydride (6·7 g.) was heated at 160° for 3·5 hours.

A xylene extract of the semi-crystalline product, when shaken with sodium carbonate, gave a copious precipitate of the sodium salt in white pearly plates. This was washed with benzene, dried at room temperature, and acidified in aqueous suspension. The *naphthyl hydrogen diphenate* (8 g., m. p. 190—198°) obtained crystallised from acetic acid in long prisms, m. p. 202—203° (Found: C, 78·1; H, 4·4. $C_{24}H_{16}O_4$ requires C, 78·3; H, 4·3%).

β-*Naphthyl hydrogen diphenate,* prepared similarly, crystallised from acetic acid in small prisms, m. p. 178—179° (Found: C, 78·2; H, 4·3%).

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THE RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, January 26th,* 1929.]

CIV.—*Diethyl Ether. Part I. The Products of its Autoxidation.*

By HAROLD KING.

FROM the observations of numerous workers it has long been established that diethyl ether may undergo change on storage with production of acetaldehyde and peroxides. It is only within the last few years, however, that any advance has been made in the elucidation of the constitution of the peroxides formed. In 1922 Clover (*J. Amer. Chem. Soc.*, **44**, 1107) published the results of a close study of the autoxidation of ether and drew the conclusion that the peroxide in ether is formed by addition of a molecule of oxygen to a molecule of ether:

$$Et{\cdot}OEt + O_2 = EtO{\cdot}CH{<}^{Me}_{O{\cdot}OH}$$

Under the action of acidified water this product undergoes irreversible hydrolysis with production of acetaldehyde, ethyl alcohol, and hydrogen peroxide:

$$EtO{\cdot}CH(O_2H){\cdot}CH_3 + H_2O = EtOH + H_2O_2 + CH_3{\cdot}CHO$$

In 1923, however, a different view was advanced by Wieland and Wingler (*Annalen*, **431**, 301), who suggested that the first action of oxygen was a dehydrogenation of diethyl ether with production of ethyl vinyl ether and hydrogen peroxide. The ethyl vinyl ether

then underwent hydrolysis with formation of ethyl alcohol and acetaldehyde :

$$EtO{\cdot}CH_2{\cdot}CH_3 + O_2 = EtO{\cdot}CH{:}CH_2 + H_2O_2$$
$$EtO{\cdot}CH{:}CH_2 + H_2O = EtOH + CH_3{\cdot}CHO$$

The acetaldehyde and hydrogen peroxide thus formed combined with production of diacetaldehyde hydrogen peroxide (di-α-hydroxyethyl peroxide),

$$2CH_3{\cdot}CHO + H_2O_2 \rightleftharpoons CH_3{\cdot}CH(OH){\cdot}O{\cdot}O{\cdot}CH(OH){\cdot}CH_3$$

the equilibrium being in favour of the right-hand side. Such a combination of aldehydes and hydrogen peroxide had been established in the analogous cases of benzaldehyde, formaldehyde, and hydrogen peroxide by Nef (*Annalen*, 1897, **298**, 292) and of chloral and hydrogen peroxide by Baeyer and Villiger (*Ber.*, 1900, **33**, 2484). Wieland and Wingler supported their view by a comparison of synthetic di-α-hydroxyethyl peroxide with the peroxide left on evaporation of rich peroxidic ethers.

The two opposing views bear this resemblance, that the simple units concerned in the changes are the same and in the same proportions. They differ in that, in the one case, the substance responsible for the peroxide reactions in deteriorated ethers is hydrolysed irreversibly to an equimolecular mixture of acetaldehyde and hydrogen peroxide (Clover), whereas, in the other, agents of hydrolysis would produce two molecules of acetaldehyde to one molecule of hydrogen peroxide (Wieland). Wieland and Wingler's proposition of di-α-hydroxyethyl peroxide as the peroxide in ether ignores the fate of the other molecule of uncombined hydrogen peroxide produced in their scheme of autoxidation of the ether molecule. The experimental results of these two groups of workers do not allow a final decision to be made as to which view is correct, and it is evident that new experimental modes of attack are necessary.

The methods which have been proposed for the estimation of peroxides in ether usually depend on the liberation of iodine from potassium iodide, and they require some time for the completion of the reaction. A rapid method giving reproducible results has now been devised depending on the liberation of hydrogen peroxide in acid solution from the peroxides and its titration by permanganate in the presence of manganese salts. It was controlled on acetaldehyde–hydrogen peroxide mixtures in ether. Using this mode of titration it is not uncommon to find Winchester-quart bottles of old ether which contain peroxides equivalent to from 3 to 6 grams of hydrogen peroxide per litre. When such ether is distilled through a column, the peroxides remain behind quantitatively, so

that accumulation of dangerous amounts of peroxides, leading to the explosions so frequently recorded in the literature, is not surprising, especially where the evaporation of large volumes of deteriorated ether is carried out.

The permanganate titration gives a measure of hydrogen peroxide either free or in labile combination. It is directly applicable to the ethereal solution, to the residue obtained on removal of the ether in a vacuum, or to the parallel products from acetaldehyde and hydrogen peroxide mixtures. It fails, however, with *s*-dihydroxydimethyl peroxide, a crystalline substance soluble in water and temporarily stable to acidified permanganate. The estimation of acetaldehyde may be effected by an application of Ripper's method (*Monatsh.*, 1900, **21**, 1079). Using these two methods, with adequate control experiments at every stage, it has been possible to throw new light on the constitution of the main peroxide in ether and to adduce evidence pointing to the existence of a second peroxide of greater stability.

A known volume of ether containing peroxide is evaporated rapidly in a vacuum desiccator over sulphuric acid. The syrupy residue is kept *in situ* for 15 to 30 minutes after all the ether has been removed; it is then dissolved in water to a known volume and an aliquot part acidified and titrated with permanganate The remainder is transferred to a flask, treated with acid, and distilled into standard sodium hydrogen sulphite solution. Th residue in the distillation flask is titrated with permanganate, an a back titration made of the sulphite in the absorption flasks wit iodine. Control experiments on pure aqueous acetaldehyde solution of concentrations comparable with those which arise in experiment with ether show agreement to within 1 or 2%. Similar experiment on ethereal solutions of acetaldehyde and hydrogen peroxide mac up in the molecular ratio 2 : 1 indicated perfect agreement betwee the two permanganate titration figures, namely, before and aft distillation, showing that there is no destruction of hydroge peroxide under the particular experimental conditions used. Mor over, the acetaldehyde : hydrogen peroxide ratio in duplica experiments was 1·83 : 1 and 1·91 : 1 instead of 2 : 1. If to th synthetic di-α-hydroxyethyl peroxide in ether, excess of acetaldehy was added and the solution kept for some hours over dry sodiu sulphate, a redetermination of the ratio of acetaldehyde to hydrog peroxide gave 2·2 : 1 and 2·1 : 1. When, however, a natu peroxide ether (*i.e.*, diethyl ether containing peroxide produced autoxidation) was submitted to the same process, the aldehy estimations proceeded normally but there was always a discrepar between the two permanganate titration figures, the one obtai

on the distillation residue being larger by about 10%. This behaviour is also met with when the ethereal solutions are submitted to a preliminary purification for removal of acetic acid and formic acid, which are always found to a small extent in the products of the autoxidation of ether. It is also independent of the sample of ether used. The results suggest the presence in peroxidised ether of a peroxide more stable than the simple additive type of compound in which acetaldehyde and hydrogen peroxide are concerned, one in which the hydrogen peroxide is revealed only after boiling with dilute sulphuric acid. The presence of *s*-dihydroxydimethyl peroxide would in many ways fit the observations, but no evidence could be found for the presence of formaldehyde in the distillate.

The results of the determination of the *acetaldehyde : hydrogen peroxide ratio* on natural peroxidic ethers, whether treated with dilute alkali to remove acids or not, indicate a much lower ratio of acetaldehyde to hydrogen peroxide than 2 : 1, and this is confirmed by allowing such ethers to react with excess of acetaldehyde; the ratio then approximates to the 2 : 1 ratio. The summary of the results for a group of ethers is shown in the following table.

Peroxidic ether.	Aldehyde : hydrogen peroxide.		
Synthetic (2 : 1)	1·91 : 1	1·83 : 1	1·82 : 1
Synthetic + acetaldehyde	2·2 : 1	2·1 : 1	
Natural B (untreated)	1·24 : 1	1·32 : 1	1·30 : 1
Natural B + acetaldehyde	2·1 : 1	2·3 : 1	
Natural X (untreated)	1·13 : 1	1·13 : 1	
Natural X + acetaldehyde	2·21 : 1		
Natural A (treated)	1·16 : 1	1·13 : 1	
Natural C (treated)	1·28 : 1		

From these results it is evident that the peroxides which develop in natural ethers, whether submitted to a preliminary treatment with weak alkali to remove acids or not, contain acetaldehyde and hydrogen peroxide approximately in the ratio 1 : 1 rather than 2 : 1, the mean of the above figures being actually 1·2 : 1. Now this ratio is that which would be produced by the breakdown of Clover's peroxide or by Wieland and Wingler's suggested mechanism for the autoxidation of the ether molecule. The observation, however, that the natural peroxidic ethers can fix more acetaldehyde when it is added to their solutions, and fix it, moreover, in the proportion 2 : 1, is quite incompatible with Clover's formulation of the constitution of the peroxide. It is, however, consistent with Wieland and Wingler's view that the peroxide in ether is essentially a combination of acetaldehyde and hydrogen peroxide, and it is also consistent with their view that these constituents are produced during the autoxidation of ether. Although it is true that the ethers examined above had been kept for several years for the accumu-

lation of peroxides, so that changes in the acetaldehyde : hydrogen peroxide ratio might have taken place, the available evidence points in the other direction. The formation of acetic acid, presumably by interaction between acetaldehyde and hydrogen peroxide in molecular proportion, proceeds to a small extent in comparison with the amount of acetaldehyde and hydrogen peroxide present, and would, moreover, leave the acetaldehyde : hydrogen peroxide ratio unchanged. The catalytic decomposition of hydrogen peroxide, however, would be a much more serious factor; it might incidentally account for the deficiency of hydrogen peroxide in the ratio of acetaldehyde to hydrogen peroxide found (1·2 : 1), but evidence will be forthcoming in subsequent Parts of this investigation to show that acetaldehyde has a stabilising action on hydrogen peroxide in ether.

Since it is now established that in the autoxidation of ether, acetaldehyde and hydrogen peroxide accumulate approximately in the ratio 1 : 1, the question arises whether one is dealing with a monoacetaldehyde hydrogen peroxide, or with a mixture in equimolecular proportion of hydrogen peroxide and di-α-hydroxyethyl peroxide. Without a close study of the equilibrium which exists in ethereal solution between acetaldehyde and hydrogen peroxide it is not possible to give an exact solution of this problem, but that the former view is probably correct follows from experiments on the partition coefficients of these peroxides between water and ether. In dilute solution, for example, 1%, Clover found that hydrogen peroxide was about 16 times as soluble in water as in ether, in substantial agreement with the results of Ossipoff and Popoff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 637), and in more concentrated solution, 5%, Walton and Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 633) found a coefficient of 9. For the natural peroxide in ether Clover found coefficients of 1·7 and 2·0 in favour of ether, and the present author, using synthetic di-α-hydroxyethyl peroxide containing a slight excess of acetaldehyde, finds a coefficient of 1·5 in favour of ether. With these data available, a natural, untreated peroxidic ether was rapidly washed three times with one-tenth of its volume of water, the aqueous extracts were combined, and the ratio of acetaldehyde to hydrogen peroxide was determined on the extract. The value found was 1·4 : 1, a value which is incompatible with the view that the peroxide is an equimolecular mixture of hydrogen peroxide and di-α-hydroxyethyl peroxide, but consistent with the formulation of the peroxide as mainly monoacetaldehyde hydrogen peroxide, $CH_3·CH(OH)·O·OH$.

Whilst it appears that Wieland and Wingler's view of the production of acetaldehyde and hydrogen peroxide in equimolecular

proportion during the autoxidation of ether is substantially correct, their formulation of these components as uniting with almost exclusive formation of di-α-hydroxyethyl peroxide, leaving the fate of the remaining molecule of hydrogen peroxide undecided, is, on the evidence presented here, untenable.

Woker (*Ber.*, 1914, **47**, 1024) found that a mixture of formaldehyde and hydrogen peroxide in aqueous solution had the property of giving a blue colour with benzidine without the use of peroxidase, a property not exhibited by the constituents separately. Wieland and Wingler showed, however, that the property is lost with time or on warming, and suggested that the blue colour was produced by the intermediate monoformaldehyde hydrogen peroxide and not by the final product, *s*-dihydroxydimethyl peroxide. The same has now been found to apply to acetaldehyde and hydrogen peroxide mixtures, the blue benzidine reaction of mixtures of acetaldehyde and hydrogen peroxide in the ratio 2 : 1 being initially intensely positive, but disappearing with time. The peroxide, however, from natural ether, in all the examples examined, gave a positive reaction.

To summarise, the main peroxidic constituent of deteriorated ether is monoacetaldehyde hydrogen peroxide, but there are indications of a second peroxide of more stable type.

EXPERIMENTAL.

Titration of Peroxides in Ether.—A simple and rapid method for determining the peroxide content of deteriorated ethers is the following : 5 or 10 c.c. of the ether are added to 50 c.c. of approximately *N*-sulphuric acid in a 200 c.c. bottle, followed by a few crystals of manganese sulphate. *N*/10-Potassium permanganate is then run in slowly with rotation of the contents of the bottle to ensure extraction of the peroxides by the aqueous layer. The end-point is taken when the pink colour produced by two drops of permanganate has not completely faded in 10 seconds. This gives a measure of free hydrogen peroxide or that set free from labile compounds by the acid solution. The consumption of permanganate is independent of the presence of acetaldehyde or formic acid, both of which occur in peroxide-rich ethers.

The validity of the method is shown as follows : Perhydrol (3 c.c.) was shaken once with 50 c.c. of dry ether, and the ethereal solution of hydrogen peroxide dried over sodium sulphate. The hydrogen peroxide content was determined on 5 c.c., which required 32·3 and 32·26 c.c. of *N*/10-permanganate in duplicate experiments. To the residual volume of ether (40 c.c.), acetaldehyde (slightly more than 2 mols.) was added (2 c.c.). On titration of 5 c.c. as

before, 30·93 c.c. of $N/10$-permanganate were required or 32·5 c.c. when a correction is applied for the increase of volume on addition of the acetaldehyde. When dihydroxydimethyl peroxide is added to N-sulphuric acid there is no comparable immediate consumption of permanganate.

As examples of the potential hydrogen peroxide content of deteriorated ethers the following values may be given. Four Winchester-quart bottles of methylated ether of different origin, left untouched on shelves exposed to daylight for a period not less than 4 years, gave potential hydrogen peroxide contents of A, 5·6 g.; B, 3·8 g.; C, 3·0 g.; and X, 2·8 g. per litre. These ethers had not become markedly diminished in volume by evaporation. Another much smaller bottle of ether, in which some concentration had been effected by evaporation, showed a content of 10 g. of hydrogen peroxide per litre.

Effect of Distillation on the Peroxide Content of Ether.—An ether (985 c.c.) which contained an available hydrogen peroxide content of 1·24 g. per litre was slowly distilled through an 8-bulb pear column. After the removal of 840 c.c. the residue, 145 c.c., contained available hydrogen peroxide equivalent to 8·36 g. per litre (calc., 8·42). There is thus no loss of peroxide content on distillation through an efficient column. This is also confirmed by sensitive qualitative tests for peroxides in the distillate. If, however, ether containing peroxides be distilled without a column, some peroxides pass over with the ether.

Detection of Hydrogen Peroxide in Peroxide-rich Ethers.—Severa[l] workers have recommended the chromic acid test for the detectio[n] of free hydrogen peroxide in ether. If no organic peroxides ar[e] present, one part of hydrogen peroxide in 400,000 parts of ethe[r] may be detected by the technique described below. In the presenc[e] of acetaldehyde the test is untrustworthy. The compounds forme[d] between acetaldehyde and hydrogen peroxide are so labile to acid that it is extremely doubtful whether the hydrogen peroxide detecte[d] is initially free or not. Certain substances present in peroxidi[c] ethers appear to inhibit this reaction. For instance, a natur[al] ether rich in peroxides and of known peroxide content gave a ver[y] faint blue colour, but an ether containing the same amount [of] hydrogen peroxide with one or two mols. of added acetaldehyde an[d] dried over sodium sulphate always gave a much more inten[se] reaction.

Detection of Hydrogen Peroxide in Ether.—One part of hydroge[n] peroxide in 400,000 parts of ether may be recognised by addi[ng] 9 c.c. of the ether to 1 c.c. of water to which has been added 1 dr[op] of $2N$-sulphuric acid and 1 drop 0·5N-potassium dichromate soluti[on]

and shaking the mixture in a stoppered cylinder for 30 seconds. On decanting the ethereal layer into a narrow test-tube (0·9 cm. internal diameter) and viewing the contents vertically, a faint blue colour is just recognisable and is unmistakable when compared with a control tube of pure ether. The same dilution of peroxide may be detected in 2 c.c. of ether by Jorissen's vanadic acid reagent (Baskerville and Hamor, *J. Ind. Eng. Chem.*, 1911, **3**, 301). For this purpose 0·5 c.c. of the reagent is diluted with 1·5 c.c. of water and shaken for 30 seconds in a stoppered tube with 2 c.c. of the ether under examination. A brownish-orange colour is just detectable in comparison with a control.

Synthetic Di-α-hydroxyethyl Peroxide in Ether.—Merck's perhydrol (3 c.c.) was extracted twice, each time with 50 c.c. of sodium-treated ether, and the extracts were combined and dried by addition of freshly ignited sodium sulphate. The ethereal solution (91 c.c.) was decanted into a measuring cylinder, 1 c.c. removed, and its hydrogen peroxide content determined by permanganate (Found: 1 c.c. of ether equivalent to 4·64 c.c. of $N/10$-permanganate). To the solutiou 2 mols. of acetaldehyde (2·3 c.c.) were added, followed by anhydrous sodium sulphate. When the ethereal solution was rapidly evaporated in a vacuum, di-α-hydroxyethyl peroxide was left as a clear syrup. This substance has a faint odour of acetaldehyde, but the main odour resembles that of the residue obtained on evaporation of deteriorated ethers without the pungent odour due to formic acid. Attempts to crystallise the peroxide failed, but small quantities could be distilled along a test-tube by careful application of heat.

Determination of the Ratio Acetaldehyde : Hydrogen Peroxide.—Of the above ethereal solution, 10 c.c. were transferred to a 25 c.c. standard flask and the ether was removed by evaporation at room temperature for 45 minutes in a desiccator containing sulphuric acid and evacuated by a good water-pump through a calcium chloride guard-tube. The ether had usually evaporated in 30 minutes and drying was continued for about 15 minutes. The clear syrupy residue was dissolved in water and made up to 25 c.c. with water, and an aliquot portion (10 c.c.) transferred to a small flask fitted with a dropping-funnel and delivery tube containing a spray trap. The delivery tube was attached to a water-condenser which led into three successive flasks containing 25 c.c., 20 c.c. of standard sodium hydrogen sulphite solution and 15 c.c. of saturated sodium hydrogen carbonate solution. Through the dropping-funnel 25 c.c. of $2N$-sulphuric acid and 15 c.c. of water were slowly run in and when all was added the contents of the flask were gently boiled for 20 minutes. The acetaldehyde was fixed by the sodium hydrogen sulphite and back titration with standard iodine gave

the amount of uncombined sulphite. The sodium hydrogen carbonate solution served as a trap for volatile sulphur dioxide, which usually amounted to a fraction of a c.c. of $N/10$-iodine solution. After the distillation was complete the residue in the distillation flask was cooled, diluted slightly, and titrated with standard permanganate. This gave the hydrogen peroxide content and in the case of synthetic acetaldehyde hydrogen peroxides should agree with the figure obtained by direct titration of the original 15 c.c. left after removal of the aliquot portion for distillation.

The results of such an experiment are given below. Total back titre of sodium hydrogen sulphite and sodium hydrogen carbonate, 58·37 c.c. of $N/10$-iodine; original titre of sulphite, 91·99 c.c. whence sulphite fixed by acetaldehyde is 33·62 c.c. of $N/10$-iodine Direct titration of 15 c.c. of the original peroxide solution, 27·64 c.c of $N/10$-permanganate, whence for 10 c.c., 18·43 c.c. of $N/10$-permanganate. Titration of distillation residue, 18·54 c.c. permanganate, in good agreement with the preceding value. Hence, molecules of acetaldehyde : molecules of hydrogen peroxide = 33·62 : 18·43 or 1·82. Repetition of the process gave values 1·83 and 1·91, indicating that about 93% of two molecules of acetaldehyde remain attached to one molecule of hydrogen peroxide after evaporation of the ethereal solution in the manner described above.

The quantitative estimation of acetaldehyde by this method was controlled by distillation in the same apparatus of a standard solution of comparable concentration, 0·322 g. per 100 c.c., and recovery of 0·325 g. per 100 c.c.

Effect of Excess of Acetaldehyde on the Aldehyde : Hydrogen Peroxide Ratio.—To about 25 c.c. of the above ethereal solution a further 1 c.c. of acetaldehyde was added and the solution kept over sodium sulphate. Ten c.c. were then removed and analysed in precisely the same way as described above, evaporation of the ethereal solntion being prolonged to 1 hour to effect removal of uncombined acetaldehyde. The ratios obtained in duplicate experiments were aldehyde : hydrogen peroxide = 2·2 and 2·1.

Ratio of Aldehyde to Hydrogen Peroxide in the Peroxides of Untreated Ether.—Two Winchester quarts of ether of different origin had been left exposed to daylight for several years. The aldehyde : peroxide ratio was determined as described above, but the figures require detailed consideration. For instance, 25 c.c. of an old methylated ether B were evaporated in a 50 c.c. standard flask for 90 minutes in a vacuum, removal of the ether taking 75 minutes. The volume was made up to 50 c.c. with water, 25 c.c. were transferred to the distillation apparatus, and the aldehyde was distilled after the addition of 25 c.c. of $2N$-sulphuric acid. The sulphite

consumed by aldehydes was equivalent to 41·3 c.c. of $N/10$-iodine. On direct titration of 25 c.c. of the original solution, the peroxide was equivalent to 28·53 c.c. of $N/10$-permanganate and titration of the distillation residue showed peroxide equivalent to 31·68 c.c. of $N/10$-permanganate. There is thus a discrepancy of about 10% in the two permanganate titration figures and it is always found when the residues from natural peroxidic ethers are examined. When the flask giving the low titre was kept for 30 minutes, it straightway consumed a further 0·5 c.c. of $N/10$-permanganate, indicating the generation of hydrogen peroxide from a more stable complex than di-α-hydroxyethyl peroxide. The behaviour can be imitated by adding *s*-dihydroxydimethyl peroxide to N-sulphuric acid and then adding permanganate. No reaction takes place, but with lapse of time hydrogen peroxide is slowly generated and can be titrated. If the mixture is kept for many hours, a much larger consumption of permanganate will take place immediately. The figure given by the titration of the distillation residue thus gives a more correct value for the peroxide content than the direct titration. Hence molecules of acetaldehyde : hydrogen peroxide = 41·3 : 31·68 = 1·3. In duplicate experiments, the values found were 1·24 and 1·32; mean 1·29. This indicates that only 64% of two molecules of aldehyde are present to one of hydrogen peroxide.

Another methylated ether, X, gave the molecular ratio acetaldehyde : hydrogen peroxide, 1·13 : 1 and 1·13 : 1.

An attempt to detect formaldehyde in the distillate was made by evaporating the ether from 20 c.c. of ether B and distilling the residue from N-sulphuric acid into a few c.c. of water. The distillate gave a strong aldehyde reaction with Schiff's reagent, but failed to respond to Denigès' sensitive reaction (*Compt. rend.*, 1910, 150, 529) for formaldehyde in the presence of acetaldehyde. A mixture of acetaldehyde and formaldehyde in the proportion indicated by the two permanganate titration figures, *i.e.*, approximately 90% of acetaldehyde to 10% of formaldehyde, and at a comparable dilution to the distillate readily showed formaldehyde by Denigès' test. Furthermore, *s*-dihydroxydimethyl peroxide distilled from N-sulphuric acid gave formaldehyde in the distillate.

Action of Acetaldehyde on Natural Ether Peroxides.—Several c.c. of acetaldehyde were added to 100 c.c. of ethers B and X, and the solutions kept over sodium sulphate. The aldehyde : hydrogen peroxide ratio was then determined in the usual way. For ether B, the ratios found were 2·1 : 1 and 2·3 : 1 and for ether X, 2·2 : 1.

Ratio of Acetaldehyde to Hydrogen Peroxide in Treated Peroxidic Ethers.—Two other Winchester-quart bottles of methylated ether rich in peroxides were also available and the ethers were submitted

to an initial purification. Each was slowly distilled, through a long 8-bulb pear column to prevent loss of peroxides, until the residual volume was 250 c.c. This was extracted rapidly with saturated sodium hydrogen carbonate solution to remove acids and then 40 to 50 successive small portions of water, each 10 c.c. The ether was then dried over freshly ignited sodium sulphate, and the aldehyde : hydrogen peroxide ratio determined on evaporated samples in the same way as described above. For ether A, the ratio was 1·16 and 1·13 and for ether C, 1·28. These figures confirm those obtained on untreated ethers.

Effect of Washing on the Acetaldehyde : Hydrogen Peroxide Ratio of Natural Peroxidic Ether.—Ether B (100 c.c.) was extracted rapidly three times with 10 c.c. of water each time. The aqueous layers were combined, made up to 50 c.c., and analysed in the usual way : the ratio of acetaldehyde to hydrogen peroxide was 1·43 : 1.

Distribution of Acetaldehyde between Ether and Water.—A standard solution of acetaldehyde in water, when analysed by direct addition to standard sulphite solution, was found to contain 0·256 g. in 50 c.c. Of this, 40 c.c. were added to 40 c.c. of pure diethyl ether in a graduated stoppered cylinder and the mixture was shaken and allowed to attain equilibrium at 20°. The final volumes were 43·0 c.c. of aqueous layer and 36·5 c.c. of ethereal layer. Of each, 10 c.c. were removed and the aldehyde content was determined by direct treatment with sulphite. The total amounts of aldehyde found in the two layers were in close agreement with that originally present. The ratio acetaldehyde in water to acetaldehyde in ether was 2·45 : 1.

Distribution of Di-α-hydroxyethyl Peroxide between Ether and Water.—Ether (10 c.c.) containing synthetic di-α-hydroxyethyl peroxide and a slight excess of acetaldehyde was shaken at 25° with 8 c.c. of water. The resultant volumes were each 8 c.c., and 5 c.c. of each were removed and the peroxide content was estimated by permanganate. The ether consumed 8·96 c.c., and the water 5·82 c.c., of *N*/10-permanganate, whence the distribution coefficient for di-α-hydroxyethyl peroxide is 1·5 in favour of ether.

s-Dihydroxydimethyl Peroxide, $OH{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$.—Formalin (6 c.c.) was diluted with water (18 c.c.), and perhydrol (4·5 g.) in 12 c.c. of water added. The solution was kept for 12 hours and then allowed to evaporate rapidly in a vacuum desiccator over sulphuric acid. Crystals separated on the sides of the dish and when the volume had been reduced to 2 or 3 c.c. the contents were inoculated with the crystals and kept at 0° for a few hours. *s*-Dihydroxydimethyl peroxide separated in triangular prisms, which were separated by decantation and dried on porous plate. It is very soluble in water and in agreement with the observations of Wieland and

Wingler gives no immediate reaction with Schiff's reagent, acid permanganate, or vanadic acid. It reacts with the guaiacum and benzidine reagents only on addition of peroxidase. For analysis, 0·381 g. was dissolved in 10 c.c. of water and treated with 10 c.c. of *N*-potassium hydroxide, followed by 10 c.c. of 10-volume hydrogen peroxide solution. After 15 minutes the unconsumed alkali was titrated with standard acid. The percentage of formaldehyde found was 63·5 (calc., 63·8). This confirms the view that there are two molecules of formaldehyde combined with one of hydrogen peroxide. The crystalline solid when kept in a tube develops formic acid, but if left on an open watch-glass the crystals soon disappear through volatilisation.

Stability of Hydrogen Peroxide in Boiling N-*Sulphuric Acid and its Volatility in Steam.*—A determination was made to ascertain the loss which occurred on distillation of weak solutions of hydrogen peroxide in *N*-sulphuric acid. Of such a standard solution, 50 c.c. were distilled for 20 minutes through the usual apparatus fitted with an anti-splash device, the volume diminishing by a third to a half. On determining the peroxides in the two fractions, distillate and residue, 1·9% was found in the distillate and 2·1% had been destroyed. In a duplicate experiment with 0·5*N*-sulphuric acid, the volatile peroxide was 0·6% and that destroyed 3·6%.

Acidity of Peroxidised Ethers.—The presence of acetic acid in ether that has undergone autoxidation was observed by Richardson and Fortey (P., 1896, 165), but the formation of formic acid appears to have been overlooked. The latter can readily be detected by its very pungent odour and by its reducing properties on mercuric chloride, mercuric acetate or silver nitrate solution. Attempts to estimate the relative proportion of acetic and formic acids by use of methods depending on the formation of mercurous acetate or chloride proved untrustworthy. The total acidity in comparison with the peroxide content was determined on two ethers which had undergone autoxidation for several years. For ether B, 10 c.c. required 2·74 c.c. of *N*/10-sodium hydroxide for neutralisation to phenolphthalein and the peroxide content was equivalent to 28·9 c.c. of *N*/10-permanganate. If the acidity arises entirely from the oxidising action of hydrogen peroxide on aldehydes, this corresponds to a 15·9% conversion of hydrogen peroxide. For ether X, 10 c.c. required 0·72 c.c. of *N*/10-sodium hydroxide and the peroxides required 19·8 c.c. of *N*/10-permanganate. This corresponds to a 6·8% conversion of hydrogen peroxide. Whether the formic acid arises by oxidation of methylated ethers present in the original ether or by oxidation of the vinyl alcohol form of acetaldehyde is not known.

The Guaiacum and Benzidine Tests for Peroxides.—For these tests a freshly prepared 10% alcoholic tincture of guaiacum and a 1% solution of benzidine in 50% alcohol were used. Pure crystalline dihydroxydimethyl peroxide in aqueous solution gives no coloration on addition of the guaiacum or benzidine reagent, but a blue colour is immediately produced on addition of a dilute solution of peroxidase (from horse-radish) to either. Di-α-hydroxyethyl peroxide obtained as a syrup by evaporation of an ethereal solution of the components containing a slight excess of acetaldehyde gives no coloration in aqueous solution with the same reagents, but does so on addition of peroxidase. Fresh aqueous solutions of formaldehyde or acetaldehyde and hydrogen peroxide in the ratio 2 : 1, however, both give a direct reaction with the benzidine reagent without the use of peroxidase, but not with guaiacum. In both cases this reaction becomes negative when the solutions are kept for 2 or 3 days. A similar direct benzidine reaction is obtained when a natural peroxidic ether is evaporated and the aqueous solution of the residual peroxide tested with the benzidine reagent.

The results are consistent with the view that the direct blueing of benzidine is due to an intermediate peroxide containing the aldehyde and hydrogen peroxide in molecular proportion.

Laboratory samples of heptaldehyde and benzaldehyde suspended in water gave the direct benzidine reaction without addition of hydrogen peroxide, owing to their content of peroxides. It is also of interest that butyl, *iso*octyl and amyl alcohols gave a reaction for peroxides with benzidine or guaiacum and peroxidase, but the reaction was not shown by methyl, ethyl, *iso*propyl and benzyl alcohols. In many of these reactions the enzyme peroxidase can be replaced by a drop of a solution of a ferrous or ferric salt.

NATIONAL INSTITUTE FOR MEDICAL RESEARCH,
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CV.—*Substituted Aromatic Aldehydes in Hantzsch's Pyridine Condensation. Part I. Methoxy-, Chloro-, and Hydroxy-benzaldehydes.*

By LEONARD ERIC HINKEL and WILLIAM REES MADEL.

IT has already been shown (Hinkel and Cremer, J., 1920, **117**, 137) that in Hantzsch's pyridine synthesis the introduction of a *p*-dimethylamino-group into benzaldehyde has a marked inhibitory effect upon the condensation. As no systematic study has hitherto been made involving both the nature and the position of the sub-

stituent groups in the aldehydes, condensations have been carried out under similar experimental conditions with *o*-, *m*-, *p*-methoxy-, -chloro-, and -hydroxy-benzaldehydes. Since the three substituting groups are electronegative in character, although of varying intensity, it might be expected that the results obtained with the groups in the *o*-, *m*-, or *p*-position would to some extent be comparable and that similar gradations in the yields of condensation product would be shown. From the theory of alternate polarities (Lapworth and Shoesmith, J., 1922, **121**, 1391) negative groups in the *o*- and *p*-positions should augment the activity of the aldehyde oxygen, and a negative group in the *m*-position diminish it. In all cases (Table I), however, the presence of the substituent lowers the yield of the product as compared with that from benzaldehyde, which gives a 90% yield (compare Hinkel and Cremer, *loc. cit.*).

TABLE I.

Percentage yields of dihydropyridine derivative.

Substituent.	*o*.	*m*.	*p*.
Methoxy	48	33	65
Chloro	38	78	69
Hydroxy	0	36	49

These results, apart from the general depressant effect noted above, are not in agreement with the theory of alternate polarities (Table II), but appear to be in general agreement with the depressant effects of substituents on the affinity of benzaldehyde for hydrogen cyanide as recently recorded by Lapworth and Manske (J., 1928, 2533). It would appear that the factors influencing the ionisation constants of substituted benzoic acids (Flürscheim, J., 1909, **95**, 726) affect similarly the reactivity of the aldehyde group. Since, in the above cases, the yields of dihydropyridine derivatives are smaller than the yield from benzaldehyde, the general "electropolar" factor of each of the three substituents is more pronounced than the "quantitative" factor. The quantitative factor is least pronounced in the case of chlorine, since the *m*- and *p*-chloro-deriv-

TABLE II.

Substituent.	Comparison.	Agreement (+) or reverse (−) with deduction from polarity standpoint.
Methoxy	*m* and *o*	+
	m ,, *p*	+
Hydroxy	*m* ,, *o*	−
	m ,, *p*	+
Chloro	*m* ,, *o*	−
	m ,, *p*	−

atives show the least difference in yield. Further, the quantitative factor for chlorine is unexpectedly exerted in the opposite sense to those for the methoxy- and the hydroxy-group, since with these the yield of the *m*-derivative is less than that of the *p*-derivative, which is the reverse of that found with chlorine. The influence of the steric factor is seen in the decreased yields of *o*-chloro- and *o*-methoxy-derivatives as compared with the corresponding *p*-derivatives. The abnormal behaviour of *o*-hydroxybenzaldehyde would be expected from the conclusions of Sidgwick and Callow (J., 1924, **125**, 527), that co-ordination occurs between the hydroxy- and the aldehyde group, the typical properties of each group being diminished.

With the exception of the derivatives of the hydroxy-aldehydes, the oxidation of the dihydropyridine compounds proceeded normally and in no case was there any apparent tendency for the elimination of the phenyl group. The dihydropyridine derivatives from the hydroxy-aldehydes, owing to their phenolic character and tendency to form nitroso-compounds, do not lend themselves to the normal oxidation by means of nitrous fumes.

EXPERIMENTAL.

Ethyl 4-p-*Methoxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—A mixture of 10 g. (1 mol.) of *p*-methoxybenzaldehyde, 19·2 g. (2 mols.) of ethyl acetoacetate, and 20 c.c. of alcohol was saturated with ammonia gas and, after remaining at the ordinary temperature for an hour, heated on a water-bath for several hours. (This procedure was adopted in all subsequent condensations, in which, therefore, only the treatment of the product will be described.) The yellow solid obtained on cooling crystallised from alcohol in almost colourless tetrahedra (17 g.), m. p. 159° (Found: C, 66·3 H, 7·1; N, 4·0. $C_{20}H_{25}O_5N$ requires C, 66·8; H, 7·0; N, 3·9%).

Ethyl 4-p-*Methoxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* —The dihydro-ester was made into a thin paste with alcohol and nitrous fumes were led into the mixture until a clear solution wa obtained. The greater portion of the alcohol was removed b evaporation and the residue was neutralised with sodium carbonat solution and extracted with ether (this procedure was adopted i all subsequent oxidations). The solid obtained after removal (the ether slowly crystallised from light petroleum (b. p. 40—60' in colourless rhombohedra, m.p. 50° (Found: C, 66·6; H, 6· $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%).

Ethyl 4-o-*Methoxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : *dicarboxylate*.—The condensation product from 10 g. of *o*-methox benzaldehyde was concentrated on a water-bath. The solid o

tained on cooling and stirring, after being washed with benzene, crystallised from alcohol in small yellow needles (12 g.), m. p. 151° (Found : C, 68·8 ; H, 7·1 ; N, 4·2%).

Ethyl 4-o-*methoxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in colourless stout needles, m. p. 65° (Found : C, 66·7 ; H, 6·6%).

Ethyl 4-m-*Methoxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The viscous product obtained from the condensation of 10 g. of *m*-methoxybenzaldehyde became semi-solid on standing. It was stirred with a small quantity of benzene, collected, and washed with light petroleum (b. p. 40—60°); when these washings were added to the benzene filtrate, more of the solid was obtained. It crystallised from aqueous alcohol in clusters of very small, colourless needles (9·2 g.), m. p. 120° (Found : C, 66·9 ; H, 7·3%).

Ethyl 4-m-*methoxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* crystallised from aqueous alcohol in colourless mica-like plates, m. p. 82° (Found : C, 67·3 ; H, 6·7%).

Ethyl 4-p-*Chlorophenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The crude product obtained from 14 g. of *p*-chlorobenzaldehyde deposited crystals on cooling which separated from alcohol in almost colourless, flat tetrahedra (25 g.), m. p. 149° (Found : Cl, 9·3. $C_{19}H_{22}O_4NCl$ requires Cl, 9·75%).

Ethyl 4-p-*chlorophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* crystallised from light petroleum (b. p. 60—80°) in colourless thick prisms, m. p. 68° (Found : Cl, 9·4. $C_{19}H_{20}O_4NCl$ requires Cl, 9·8%).

Ethyl 4-o-*Chlorophenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The viscous mass obtained from 14 g. of *o*-chlorobenzaldehyde was stirred with a small quantity of benzene. The fine solid which separated was removed, and a further yield obtained by the gradual addition of light petroleum (b. p. 40—60°) to the filtrate. The solid crystallised from aqueous methyl alcohol in cubes (12·6 g.), m. p. 132° (Found : Cl, 9·5%).

Ethyl 4-o-*chlorophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* crystallised from light petroleum (b. p. 40—60°) in colourless rhombohedra, m. p. 62° (Found : Cl, 9·8%).

Ethyl 4-m-*Chlorophenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The product obtained from the condensation of 14 g. of *m*-chlorobenzaldehyde solidified completely on cooling. It crystallised from aqueous methyl alcohol in stellate clusters of needles (32 g.), m. p. 142° (Found : Cl, 9·4%).

Ethyl 4-m-*chlorophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate* crystallised from methyl alcohol in colourless tetrahedra, m. p. 53° (Found : Cl, 9·5%).

Ethyl 4-p-*Hydroxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The viscous condensation product obtained from 10 g. of *p*-hydroxybenzaldehyde slowly set to a semi-solid mass. This was slightly diluted with aqueous alcohol, and the solid removed; more was obtained from the concentrated filtrate on treatment with aqueous alcohol. The solid crystallised from alcohol in clusters of fine prisms (13·3 g.), m. p. 227° (Found: C, 65·8; H, 6·8. $C_{19}H_{23}O_5N$ requires C, 66·1; H, 6·7%).

Ethyl 4-m-*Hydroxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*.—The product from 10 g. of *m*-hydroxybenzaldehyde solidified almost completely on being cooled and stirred and was then treated with aqueous alcohol as described above. The solid obtained crystallised from alcohol in small thick prisms (10·2 g.), m. p. 202° (Found: C, 66·0; H, 6·6%).

UNIVERSITY COLLEGE, SWANSEA. [*Received, January 17th, 1929.*]

CVI.—*The Determination of the Parachors of Substances in Solution.*

By DALZIEL LLEWELLYN HAMMICK and LESLIE W. ANDREW.

IT has hitherto been possible to determine the parachors only of suc substances as are capable of stable existence above their meltin points. This limitation would be removed if it could be show that the parachors of substances unstable in the pure liquid stat can be calculated from the surface tensions and densities of their sol tions in solvents of known parachor. Numerous data as to the surfa tensions and densities of liquid mixtures exist, but they are by r means equally trustworthy as to surface tensions. We have ther fore determined the surface tensions of a preliminary series of liqu mixtures, using Sugden's apparatus (J., 1924, **125**, 27) standardis with pure benzene; our data are thus on the same basis as Sugden being dependent upon the surface tension of benzene as determin by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) a confirmed by Sugden (J., 1921, **119**, 1483) using his own form apparatus with jets of experimentally determined diameter. T surface tension of benzene at 25° was taken as 28·23 dynes/cm.

In choosing the components of our mixtures, we have sought vary not only their chemical nature but also the difference betw the surface tensions of the pure substances, in order that any effe due to surface absorption might be detected. The mixtures exa ined will be seen to include cases of non-associated liquids w non-associated, associated with associated, and non-associated w associated.

Parachors of solutes have been calculated from our results by first finding the parachor P_m of a solution containing a molecular fraction x of solute in a solvent of known parachor P; P_m is equal to $M_m\gamma^{\frac{1}{4}}/(D - d)$, where γ and D are the surface tension and density of the solution, and M_m is the mean molecular weight of the mixture*; d, the density of the vapour, is negligible at 25°. On the assumption that parachors obey the straight-line mixture law, P_x, the parachor of the solute, is found from P and P_m by means of the relation $P_m = P(1 - x) + P_x . x$.

Experimental.

It is clear that the above method of calculation, particularly when it is applied to dilute solutions, requires that all experimental data should be as accurate as possible. All the liquids used were therefore very carefully purified by distillation or freezing out, particular care being taken with the benzene (m. p. 5·40°) used for standardising the apparatus employed in the determination of surface tensions. This was of the usual Sugden type (*loc. cit.*, p. 28), used in conjunction with a water or xylene manometer immersed in the thermostat (25°) that also contained the bubbler. This arrangement was found to give more concordant bubble-pressure readings than an alcohol manometer in an athermostatic water-bath as used by Sugden. The irregularities noticed by Sugden in the working of water manometers due to fouling of the water surface (*ibid.*, p. 28) were prevented by introducing tubes containing activated charcoal between the manometer and the bubbler. Pressure differences were measured by means of a cathetometer reading to 0·01 mm.; successive readings were consistent to at most 0·2%. The apparatus was restandardised before each mixture was investigated.

The following constants were used in the calculation of the parachors of solvent liquids:

H = 17·1, C = 4·8, N = 12·5, O = 20·0, Cl = 54·3, double bond = 23·2, semipolar bond = − 1·6, 6-membered ring = 6·1, carboxyl O_2 = 60·0.

Densities were determined by means of a 10 c.c. specific gravity bottle.

Our experimental results (at 25°) and calculations are summarised in the following tables, which include data (marked S. and J.) due to Sugden and W. W. Jones (private communication) for mixtures of chloroform and benzene, nitrobenzene and benzene, and nitrobenzene and carbon tetrachloride at 25·5°.

* $M_m = M_s(1 - x) + M_x . x$, where M_s is the molecular weight of the solvent, M_x that of the solute, and x is the molecular fraction of solute.

A. *Non-associated solutes in non-associated solvents.*

Carbon tetrachloride in benzene.*

x.	D.	γ.	P_m.	P_x.
0·3419	1·130	27·69	211·1	219·2
0·4512	1·208	27·74	213·3	220·8
0·7326	1·405	26·98	216·8	220·2
0·8527	1·487	26·64	218·0	220·0
1·0000	1·585	26·20	—	(219·5)

Mean P_x = 220·1, P_{CCl_4} = 219·5, $P_{calc.}$ = 222·0.

m-Xylene in benzene.

x.	D.	γ.	P_m.	P_x.
0·3969	0·8626	28·00	238·4	286·3
0·4655	0·8615	27·92	243·2	284·5
0·6918	0·8579	28·11	261·5	285·6
0·8428	0·8569	27·85	272·6	284·7
1·0000	0·8557	30·45	—	(285·1)

Mean P_x = 285·3, $P_{m\text{-}C_8H_{10}}$ = 285·1, $P_{calc.}$ = 285·1.

* Parachor of benzene = 207·1.

*cyclo*Hexane in benzene.

x.	D.	γ.	P_m.	P_x.
0·2963	0·8330	26·41	217·1	240·9
0·3790	0·8230	25·81	219·9	240·8
0·4508	0·8168	25·84	222·3	240·9
0·5240	0·8097	25·65	225·6	240·3
0·6207	0·8007	25·36	229·1	242·5

Mean P_x = 241·1, $P_{C_6H_{12}}$ = 240·1.

Chloroform in benzene.

x.	D.	γ.	P_m.	P_x.
0·2474	1·008	27·78	201·0	182·4
0·3501	1·067	27·64	198·9	183·3
0·5343	1·177	27·10	193·9	182·5
0·7365	1·303	27·34	190·4	184·3
0·9020	1·409	26·53	185·6	183·2
1·0000	1·476	26·73	—	(183·4)

Mean P_x = 183·1, P_{CHCl_3} = 183·4, $P_{calc.}$ = 184·8.

Ethyl acetate in carbon tetrachloride.†

x.	D.	γ.	P_m.	P_x.
0·1755	1·461	25·59	219·2	215·4
0·3196	1·360	25·02	218·4	215·1
0·4758	1·252	24·39	217·6	216·0
0·6884	1·105	23·96	217·4	216·1
1·0000	0·8938	23·42	—	(216·1)

Mean P_x = 215·7, $P_{CH_3\cdot CO_2Et}$ = 216·1, $P_{calc.}$ = 216·0.

Chloroform in benzene (S. and J.).

x.	D.	γ.	P_m.	P_x.
0·2068	0·9866	28·06	—	184·7
0·3966	1·0958	27·36	—	181·6
0·4892	1·1506	27·32	—	183·5
0·7096	1·2882	26·91	—	183·5
1·0000	1·4794	26·43	—	(183·0

Mean P_x = 183·3, P_{CHCl_3} = 183·0, $P_{calc.}$ = 184·8.

† Parachor of carbon tetrachloride = 220·0.

B. *Associated solutes in non-associated solvents.*

Ethyl alcohol in benzene.

x.	D.	γ.	P_m.	P_x.
0·237	0·8578	27·38	187·8	125·5
0·421	0·8422	25·40	172·1	124·1
0·564	0·8304	25·00	161·4	126·0
0·758	0·8163	23·84	145·4	125·7
1·000	0·7898	21·90	—	(126·0)

Mean P_x = 125·3, P_{EtOH} = 126·0, $P_{calc.}$ = 132·2.

Acetic acid in benzene.

x.	D.	γ.	P_m.	P_x.
0·279	0·9005	28·08	186·6	133·[illegible]
0·510	0·9329	27·04	168·9	132·[illegible]
0·820	0·9965	27·78	145·6	132·[illegible]
1·000	1·051	28·52	—	(132·[illegible]

Mean P_x = 132·5, P_{HAc} = 132·2, $P_{calc.}$ = 141·2.

Acetone in benzene.

x.	D.	γ.	P_m.	P_x.
0·2993	0·8507	26·82	193·1	159·5
0·5283	0·8318	25·52	182·4	160·3
0·7034	0·8163	24·52	174·5	160·6
0·8563	0·8017	23·67	167·6	161·1
1·0000	0·7867	22·72	—	(161·1)

Mean P_x = 160·5, $P_{C_3H_6O}$ = 161·1, $P_{calc.}$ = 160·2.

C. *Non-associated liquid in associated solvent.*

Ethyl acetate in acetic acid.

x.	D.	γ.	P_m.	P_x.
0·0000	1·0510	28·52	132·2	—
0·1273	1·0200	27·49	142·8	216·0
0·3031	0·9844	26·56	157·9	217·2
0·5429	0·9471	25·21	178·0	216·5
0·6890	0·9288	25·05	191·1	217·6
1·0000	0·8938	23·42	—	(216·1)

Mean P_x = 216·8, $P_{CH_3 \cdot CO_2Et}$ = 216·8, $P_{calc.}$ = 216·0.

D. *Associated liquids in associated solvents.*

Acetic acid in ethyl alcohol.

x.	D.	γ.	P_m.	P_x.
0·0000	0·7898	21·90	126·0	—
0·2262	0·8540	24·06	127·7	133·5
0·4241	0·9062	25·75	129·3	133·8
0·5550	0·9384	26·07	129·3	131·9
0·7414	0·9868	27·10	130·4	131·9
1·0000	1·051	28·52	—	(132·2)

Mean P_x = 132·8, P_{HAc} = 132·2, P_{calc} = 141·2.

Acetone in ethyl alcohol.

x.	D.	γ.	P_m.	P_x.
0·0000	0·7898	21·90	(126·0)	—
0·1879	0·7902	22·12	132·6	161·2
0·4508	0·7900	22·85	142·4	162·4
0·6874	0·7892	22·63	150·1	161·1
1·0000	0·7882	23·07	—	(161·4)

Mean P_x = 101·6, P_{calc} = 160·2.

Acetone in acetic acid.

x.	D.	γ.	P_m.	P_x.
0·0000	1·0510	28·52	(264·4)	—
0·2909	0·9996	27·79	234·0	160·8
0·4998	0·9547	26·74	212·1	160·3
0·6183	0·9247	26·14	199·8	160·2
0·7288	0·8921	25·53	188·5	160·5
1·0000	0·7867	22·72	—	(161·1)

Mean P_x = 160·5, $P_{C_3H_6O}$ = 161·1, $P_{calc.}$ = 160·2.

In the last example the molecule of acetic acid has been taken as $(CH_3 \cdot CO_2H)_2$, for which the parachor is 2 × 132·2 = 264·4.

In all the examples so far quoted it will be noticed that the parachor of the solute, as calculated by application of the mixture law from the mean parachor of the solution, is in good agreement with the experimentally determined parachor of the pure solute; it is, moreover, independent of the dilution. We have, however, found cases where the value of the solute parachor falls off linearly with dilution. Data for these cases are given below and are plotted in Fig. 1.

Nitrobenzene in benzene.

x.	D.	γ.	P_m.	P_x.
0·2129	0·9517	30·26	215·9	249·0
0·3707	1·0070	31·99	223·8	252·0
0·4822	1·0435	33·15	229·6	253·7
0·6109	1·0860	35·24	236·8	255·7
0·7063	1·1130	36·51	242·6	257·4
1·0000	1·1988	42·87	—	(262·5)

$P_{calc.}$ = 264·1.

Nitrobenzene in benzene (S. and J.).

x.	D.	γ.	P_m.	P_x.
0·0000	0·8722	28·23	(207·1)	—
0·1650	0·9334	30·22	—	256·4
0·3000	0·9929	31·64	—	246·9
0·5176	1·0538	34·30	—	257·2
0·7669	1·1308	38·12	—	259·6
1·0000	1·1986	43·25	—	(263·0)

$P_{calc.}$ = 264·1.

Nitrobenzene *in carbon tetrachloride* (S. and J.).

0·0000	1·5839	26·10	—	—
0·2246	1·4978	28·35	—	249·5
0·4276	1·4188	30·68	—	251·9
0·6551	1·3302	34·54	—	256·2
0·8181	1·2668	37·91	—	259·1
1·0000	1·1986	43·25	—	(263·0)

$P_{calc.}$ = 264·1.

Acetophenone in benzene.

0·1538	0·9030	29·94	219·1	284·7
0·2966	0·9279	31·13	230·4	285·6
0·4668	0·9548	32·63	244·5	287·4
0·7749	0·9975	36·06	271·6	290·4
1·0000	1·0243	38·77	—	(292·4)

$P_{calc.}$ = 294·1.

Nitromethane in benzene.

0·2327	0·9120	29·14	188·8	128·0
0·3737	0·9396	29·35	177·6	128·1
0·5594	0·9822	30·04	163·3	128·9
0·7362	1·0317	31·76	150·8	130·6
1·0000	1·1315	35·80	—	(131·8)

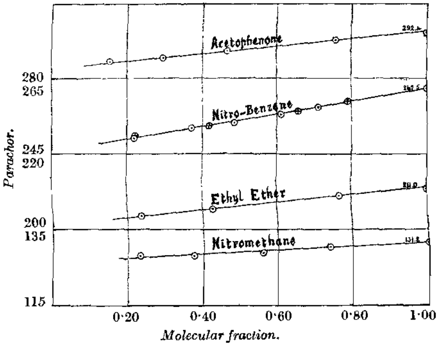
$P_{calc.}$ = 130·2.

Ethyl ether in benzene.

0·2356	0·8321	24·53	206·3	203·7
0·4267	0·7996	21·81	206·5	205·5
0·7464	0·7475	18·49	208·4	208·8
1·0000	0·7069	16·47	—	(211·0)

$P_{calc.}$ = 210·2.

Fig. 1.



The open circles in the above diagram refer to our values for solute parachors in benzene solution; Sugden and Jones's data for nitrobenzene in carbon tetrachloride are shown with crossed circles. In all cases the straight line through the solute parachor values passes through the parachor value of the pure solute to within less than 1%.

It will be seen from the above tables that the mixtures from which we have obtained solute parachor values that are independent of dilution are characterised by the fact that the surface tensions of the pure components do not differ by more than about 5—6 dynes/cm. at most. The smallest deviation from the rigid straight-line [illegible] line is found in the case of nitromethane and benzene,

where the difference in surface tension between the two components is nearly 7 dynes/cm.; the greatest deviation occurs with nitrobenzene and benzene, where the difference in surface tensions is about 14·5 dynes/cm. It is thus probable that the deviation is connected with the Gibbs surface absorption effect, and we are at present investigating the point. On the purely practical side, however, the position appears to be as follows: Application of the mixture law to the mean parachor of a series of solutions will give either the parachor of the pure solute or a series of values from which a value for the pure solute can be obtained by straight-line extrapolation. (With water as solvent anomalous results are obtained; these are being investigated.)

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THE DYSON PERRINS LABORATORY,
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CVII.—*Low-temperature Oxidation of Hydrocarbons. Part I. The Pressure–Temperature Curves of Amylene–Oxygen Mixtures.*

By J. STANLEY LEWIS.

IN a previous paper (J., 1927, 1555) the author described the effect of increase of temperature on mixtures of paraffin hydrocarbons and oxygen kept at constant volume, and suggested that the primary reaction was a dehydrogenation of the hydrocarbon, yielding water and an unsaturated hydrocarbon, which, owing to its instability in the presence of oxygen, might yield peroxides or their decomposition products such as aldehydes. The view that peroxides or moloxides are first produced by the direct union of the paraffin with oxygen during initial combustion has many supporters, and a brief review of this subject is given by Brunner and Rideal (J., 1928, 1162). They are of opinion that moloxides are initially produced at surfaces until the concentration rises to a certain critical value, whereupon chain reactions set in, accompanied by an enormous increase in the velocity of reaction.

It has been shown by the author (*loc. cit.*) that paraffin hydrocarbons possess a characteristic initial temperature of oxidation which is lower the higher the molecular weight. In the case of *n*-hexane, this is 232°, and it was found that this temperature varied only slightly with wide variations in concentration and rate of

heating. By maintaining a constant temperature somewhat below 232°, Brunner and Rideal were able to identify a preliminary slow oxidation period. Their pressure–time curves indicate a period of steady fall in pressure at constant temperature, followed by an abrupt rise in pressure. The first portion of the curve is interpreted as an induction period during which slow autoxidation occurs with the formation of moloxides or peroxides, and the final part corresponds to a period of rapid combustion or decomposition of peroxides. The predominating reactions are given as follows (J., 1928, 2824) :

$$C_6H_{14} + O_2 \longrightarrow C_6H_{14}O_2 \text{ (active moloxide)},$$
$$C_6H_{14} + C_6H_{14}O_2 \longrightarrow 2C_6H_{12} + 2H_2O,$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition}.$$

The catalytic action of water in the initial oxidation of saturated hydrocarbons has been demonstrated previously (Lewis, *loc. cit.*), and the above actions could be equally well explained by assuming in the first place that the per- or mol-oxide of hydrogen is produced by surface action, thus :

$$2H_2O + O_2 \longrightarrow 2H_2O_2 \text{ (peroxide)},$$
$$C_6H_{14} + H_2O_2 \longrightarrow C_6H_{12} + 2H_2O,$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition}.$$

There is also a possibility that the peroxide of the unsaturated hydrocarbon, if formed, might accelerate the reaction according to the equation $C_6H_{12}O_2 + 2C_6H_{14} \longrightarrow 3C_6H_{12} + 2H_2O$. This would have the merit of being in accordance with facts, for it is well known that the olefins and diolefins accelerate the oxidation of the paraffins.

The practical evidence that moloxides of saturated hydrocarbons exist is very scanty and far from conclusive. This is not the case with the olefins and dienes, which form addition products with oxygen at room temperature as shown by Engler and Weissberg (*Ber.*, 1900, **33**, 1094) in their work on autoxidation. Amylene, when allowed to stand in air in diffused daylight, gave a syrupy liquid containing oxygen of which 45% was peroxide. Trimethylethylene yielded a similar product with 30% of peroxide oxygen, and hexylene 7·2% after exposure to oxygen for 48 hours. These peroxides are unstable and under certain conditions have been known to detonate, but during slow decomposition they give rise to aldehydes, acids, carbon monoxide and dioxide, water, traces of unsaturated hydrocarbons, and hydrogen. This important point is referred to again in the discussion (p. 764).

The author still adheres to his original suggestion that the first well-defined stage in the oxidation of a paraffin hydrocarbon is the production of unsaturated hydrocarbon and water. Experimental

evidence shows that the ease with which the hydrogen is removed varies with the structure of the hydrocarbon, and the various cases which present themselves have been mentioned already (Lewis, J., 1927, 1569). Moreover, it is possible to obtain unsaturated hydrocarbons from the paraffins by partial oxidation under special conditions: by passing a mixture of pentane or hexane and air over feebly ignited platinum, Stepsky (*Monatsh.*, 1902, **23**, 773) obtained amylene and hexylene amongst the oxidation products.

A comparison of the action of sulphur and of oxygen in the removal of hydrogen from saturated hydrocarbons apparently strengthens the case for primary dehydrogenation. In some experiments made by the author, hexane vapour was drawn through molten sulphur at about 350° by a current of nitrogen, and a high yield of hydrogen sulphide was obtained. The unattacked hexane recovered was found to contain 1—2% by volume of unsaturated hydrocarbons, whilst the product in the reaction vessel was a black asphaltic mass, which was not investigated. When the hydrocarbon was heated with sulphur in an atmosphere of nitrogen in a glass bulb with a manometer attached, a rapid action, denoted by pressure increase, occurred above 320°, and after the contents of the bulb had been cooled, qualitative tests indicated the presence of hydrogen sulphide and of organic sulphur compounds which gave precipitates with mercuric chloride. Spanier had previously stated that sulphur had no action on *n*-hexane when heated at 210° for 24 hours in a sealed tube. It is suggested that the mechanism of the reaction is similar to the oxidation of the paraffin whereby hydrogen atoms of the hydrocarbon are directly removed by the sulphur, yielding more active unsaturated residues. Under the conditions of temperature and pressure of the author's experiments, the paraffins can dissociate to unsaturated hydrocarbons plus hydrogen atoms, but with negligible velocity except at the surface of the containing vessel. These hydrogen atoms may then react with oxygen or sulphur, and for the former element some such sequence as the following may occur:

$$C_6H_{14} \rightleftharpoons C_6H_{12} + 2H \text{ (surface action)},$$
$$2H + O_2 \longrightarrow H_2O_2,$$
$$H_2O_2 \longrightarrow H_2O + O \text{ (assists primary dehydrogenation)}.$$

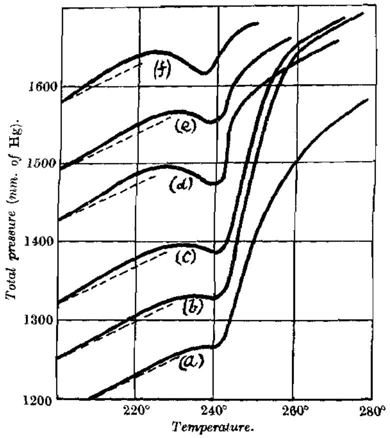
It being assumed that the initial stage of the oxidation of paraffins is the production of unsaturated hydrocarbons, the next step in the combustion may be a reaction between these hydrocarbons and oxygen. The chemical changes involved appear to be well defined, and the trend of evidence is in favour of initial peroxidation with subsequent decomposition and further oxidation. The present

paper contains an account of some work carried out on mixtures of amylene and oxygen heated continuously with moderate rise in temperature at constant volume. The changes discerned in similar mixtures maintained at constant temperature and volume will be described in a later communication.

EXPERIMENTAL.

Pressure–temperature Curves.—The hydrocarbon used in the following experiments was amylene, which was found to give a

FIG. 1.



characteristic curve. It was washed with acidified potassium iodide and redistilled after drying over calcium chloride, the fraction of b. p. 34—35° being accepted. The apparatus was a slight improvement of the one used in the experiments on saturated hydrocarbons (*loc. cit.*), in which a reaction bulb (of 225 c.c. capacity) was attached to a mercury manometer by means of a capillary tube. During the heating of the bulb, the mercury was maintained at a definite mark in the capillary tube by raising the manometer, and the height of mercury above this mark plus the barometric pressure gave the pressure of the bulb contents. Typical pressure–temperature curves are given in Fig. 1. In order that reproducible results may be

obtained it is essential that the amylene be freshly distilled and that moisture be absent. Before each experiment the bulb was washed with chromic acid, water, and alcohol, dried in an oven at about 150° whilst a current of dry air was blown into it, cooled in a desiccator, and filled with dried carbon dioxide-free oxygen. The form of the curve is not greatly affected by fairly wide variations in the rate of heating, but for very slow rates the slope is somewhat greater than for rapid heating. The above curves were obtained when a temperature of 240° was attained after approximately 2½ hours' heating. The dotted lines in Fig. 1 show the slope of an amylene–nitrogen curve for comparison. In Table I will be found the composition of the mixtures for each of the several curves. The initial part of the curve of a weak mixture (*a*) changes almost in accordance with the gas laws, but in the case of (*d*), with a composition approximating to $C_5H_{10} + O_2$, there is a maximum deviation. Analysis of mixtures during this part of the heating afforded positive information of slight chemical action occurring, carbon oxides as well as aldehydes being present at 190°.

The second part of these curves is characterised by a fall in pressure until a minimum point is reached, indicating that a slow chemical action is proceeding with a decrease in the number of molecules present. The temperature of minimum pressure varies to a small extent with the concentration of amylene and with the total pressure; thus, for mixture (*a*) the minimum point is at 241°, but it gradually falls to 237° for mixture (*f*). It will be observed that the contraction is greatest in the case of the equimolecular mixture (*d*).

TABLE I.

	Amylene, % by vol.	Residual gas at *N.T.P.* *after* oxidation.	Gas analysis, %.			% Amylene (by wt.) *oxidised to* CO and CO_2.
			CO_2.	CO.	O_2.	
(*a*)	17·8	142 c.c.	31·0	30·8	18·2	44·3
(*b*)	25·8	137 ,,	35·0	35·1	4·9	32·4
(*c*)	35·3	112 ,,	33·3	39·5	3·7	22·5
(*d*)	46·7	100 ,,	35·2	42·3	2·7	16·0
(*e*)	54·9	86 ,,	36·6	43·1	2·2	13·5
(*f*)	62·2	72 ,,	37·4	45·6	1·1	8·6

Continued heating above the point of minimum pressure is accompanied by a sharp rise in pressure due to rapid oxidation of products formed during the fall of pressure, after which the curve proceeds almost in accordance with the gas laws. A significant feature of this portion of the curves is that they are comparable with those of the paraffin series, especially as regards the influence of oxygen content, which produces a proportionate increase of pressure after the period of decomposition is complete (Brunner and Rideal, *loc.*

cit., p. 1165). This similarity is more evident when the initial oxidation products are compared, for both in the oxidation of amylene and in the induction period of *n*-hexane these contain high percentages of aldehydes, acids, and polymerised products prior to the rapid rise in pressure. A further noteworthy point concerning the curves for high concentrations of amylene is that after the temperature of minimum pressure is passed, the rise is comparatively small, and the final portion of the curve proceeds according to the gas laws but at a lower level than the initia line, thus denoting the presence of fewer molecules than in th original mixture. Therefore, whatever products may be formed during the initial slow oxidation and fall of pressure, they are comparatively stable, and if all the oxygen has been removed durin their formation they undergo little decomposition at slightly highe temperatures. It is unlikely that these compounds are peroxides which on account of their instability would readily decompose wit a much greater increase of pressure, and yield oxides of carbon. I the presence of excess of oxygen these initial products are rapidl oxidised at or above a certain critical temperature which is character ised by a minimum point in the curves, and the extent of oxidation i dependent on the amount of available oxygen (see Table I). Thes suggestions receive confirmation from chemical analysis. In th case of rich amylene mixtures the final products were mostly high boiling liquids which included aldehydes, and the total amount c carbon monoxide and dioxide was small, whereas the final product with a high oxygen content contained a very much higher percentag of these oxides.

It is very significant that the products of the above mixtures especially when the amylene ratio is large, are identical with thos obtained by the slow decomposition of amylene peroxide, and it wa thought at first that the contraction in the curves was due to rap peroxide formation. An experiment was stopped at this junctu and the bulb cooled first in air and then in cold water, the peroxid being subsequently estimated by liberation of iodine from acidifi potassium iodide solution and titration with $N/100$-sodium thi sulphate. Although iodine was assuredly set free, the amoun were equivalent to only about 5—10% of the peroxides demand by the drop in pressure.

The following interpretation of the above facts is suggested. . low temperatures, amylene combines with oxygen to form peroxid which may either dissociate or decompose to aldehydes, etc., but these temperatures dissociation preponderates. The rate of for ation of peroxides is accelerated by rise in temperature, but this m

lead to an increase in the amount of peroxides being decomposed to aldehydes, etc., which polymerise, and so account for the fall in pressure. At a critical temperature, denoted by the minimum point of depression in the curves, there are sufficient unstable products present to set up chain reactions giving rise to rapid oxidation. Peroxides may decompose rapidly to aldehydes, etc., which, in the presence of excess oxygen and the energy of this reaction, may be oxidised to oxides of carbon and water.

The induction period of Brunner and Rideal (*loc. cit.*) may possibly be accounted for by assuming a slow primary dehydrogenation for *n*-hexane at 210°, followed by peroxidation of the unsaturated hydrocarbons produced. These peroxides may decompose in the manner suggested for amylene or accelerate the formation of unsaturated hydrocarbons (*loc. cit.*), and so increase the peroxide concentration until a limiting value is reached, whereupon the decomposition is attended with rapid oxidation in the presence of excess oxygen. For this reaction to proceed, a temperature of 210° is adequate, since it has been found by the author that the initial slow oxidation of hexylene commences at about 200°.

The oxidation of amylene has also been carried out to show the following influences.

Pressure.—A 100 c.c. cylindrical bulb (having a larger ratio of surface to volume than the 225 c.c. bulb) was used with a contained mixture of approximate composition $C_5H_{10} + O_2$, but successive mixtures were subjected to increasing initial pressure, with the following results :

Pressure (cms.) at 200°.	Result.
139·5	Curve similar to those in Fig. 1.
179·5	A slight drop in the curve at 220° ; at 239°, violent oxidation with evolution of gas at great pressure.
275·8	Explosion at 238°.

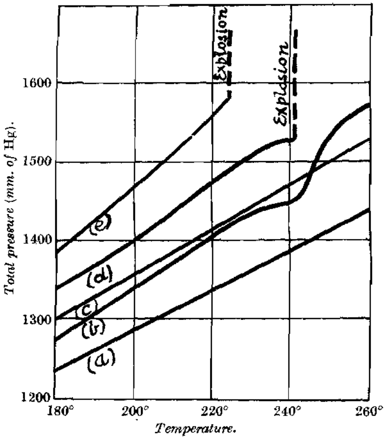
Catalysts.—The typical oxidation curves above are only obtained in the absence of water, but the result of the addition of a material quantity is seen in curve (*b*) (Fig. 2). The function of the water is probably to destroy any peroxides formed, which would account for the pressure curve being much in excess of that of the theoretical gas curve (*a*).

Inhibitors of oxidation, such as lead tetraethyl, aniline, and quinol, were found to possess the usual effect of minimising the reaction at the critical point. In curve (c), Fig. 2, the effect of the addition of 0·5% of lead tetraethyl is shown. This negative catalyst almost eliminates the contraction part of the curve, and there is apparently very little change up to 260°. An analysis of the gases

after cooling gave CO_2, 4·6; CO, 3·8%—evidence that a slow chemical action had been proceeding.

Brunner and Rideal have demonstrated that increase in active surface is an important factor in autoxidation, and that two effects were to be noted : (*i*) catalysts such as powdered glass and pumice increase the rate of peroxide formation, (*ii*) charcoal catalytically destroys peroxides. Accordingly, 1 g. of powdered pumice was heated at about the same rate as in previous experiments in a

FIG. 2.



50% amylene mixture; the curve obtained (*d*, Fig. 2) indicates progressively higher pressures than the amylene–nitrogen curve and this must be attributed to increase in velocity of oxidation due to increased surface, and this in turn may be accounted for by accelerated peroxide formation. At 234° there is a slight depression this was followed by a violent detonation at 240°, which broke the bulb and caused deposition of carbon. It is noteworthy that the temperature of explosion coincides with the minimum point in the curve of a similar mixture with pumice absent, above which temperature rapid oxidation occurs.

A mixture of amylene and oxygen can likewise be made to detonate in the presence of carbon. Curve (*e*), Fig. 2, illustrates the pressure changes on heating a 50% mixture with 1 g. of decolorising charcoal. The slope of the curve is even more pronounced than in the case of pumice, and this is probably due to the more rapid decomposition of peroxides formed with greater velocity on the surface of the charcoal. At 222° the mixture exploded, and with greater violence than in the case of pumice. This may have an important bearing on the question of detonation in internal-combustion engines, in which deposited carbon promotes pinking. A paper will be published in the near future on detonation by the above method.

Summary.

It is suggested that the second step in the combustion of a paraffin hydrocarbon is the oxidation of the primarily formed unsaturated compound to peroxide which decomposes readily, giving rise to further products (presumably aldehydes, etc.), which, in the presence of oxygen, are further oxidised to carbon monoxide and dioxide and water, owing to energy of the decomposing peroxide molecules communicated to the newly formed aldehydes, etc. Under certain conditions this action may proceed with explosive violence.

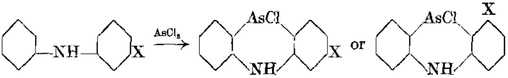
ROYAL NAVAL COLLEGE, GREENWICH. [*Received, January 16th*, 1929.]

CVIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part VII. The Synthesis of the* 1-*Methyl and* 3-*Methyl Homologues.*

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

IN the preceding parts of this series, three methods have been described for the preparation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine, *viz.*, (*a*) the condensation of substituted diphenylamines with arsenious chloride (or bromide) in the presence of a suitable solvent, (*b*) the preparation of *o*-bromo-*o'*-amino-diphenylarsinic acid, followed by the elimination of hydrogen bromide under the conditions described in Part I (*J.*, 1926, 452), yielding phenarsazinic acid, and (*c*) the preparation of substituted diphenylamine-*o*-arsinic acids on the one hand by the condensation of *o*-bromophenylarsinic acid with substituted anilines, and, on the other hand, by the condensation of *o*-aminophenylarsinic acid with

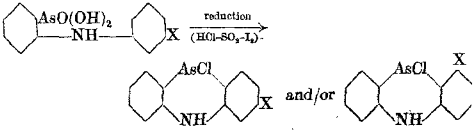
substituted bromobenzenes, followed in each case by ring closure under prescribed conditions. Some of the conditions limiting the usefulness of method (*a*) have already been mentioned (*J.*, *1926*, 2243), and method (*b*), which has not been investigated so thoroughly, is obviously limited by the practical difficulties attending the preparation of the substituted diphenylarsinic acids. Further, in method (*a*) it is obvious that, in the condensations of *m*-substituted diphenylamines with arsenious chloride, the product (if homogeneous) may have one or other of two structural formulæ :



The condensations of arsenious chloride with *m*-aminodiphenylamine (J., 1926, 2244), *m*-chlorodiphenylamine (*ibid.*, p. 2246), phenyl-β-naphthylamine (*ibid.*, p. 2243), *p*-tolyl-β-naphthylamine (*ibid.*, p. 2244), di-β-naphthylamine (*ibid.*, p. 462), and *NN'*-diphenyl-*m*-phenylenediamine (J., 1928, 2212) are instances where there is this possibility. In all these cases the condensation product appeared to be homogeneous, and, as far as this reaction is concerned, there is at present no evidence for the production of more than one product in any particular case.

In Parts IV, V, and VI of this series, the third method (*c*) of preparation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine was shown to be of general applicability. In this case also, there is the possibility that in substituted diphenylamine-*o*-arsinic acids of type (I), ring closure may lead to one or other, or both, of two isomerides :

(I.)

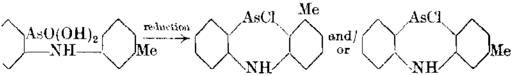


Several derivatives of 10-chloro-5 : 10-dihydrophenarsazine have already been prepared from diphenylamine-*o*-arsinic acids of type (I) by this method, and of those previously described may be mentioned the 1- or 3-carboxy- (J., 1927, 249) and the 1- or 3-nitro (J., 1928, 2514) derivatives.

The orientation of the group X in the phenarsazine nucleus find

its parallel in the work of Roberts and Turner (J., 1925, **127**, 2005) on the formation of 5 : 8-dichlorophenoxarsine from 2-*m*-chlorophenoxyphenyldichloroarsine. In this particular case, the ring compound was synthesised by a method which leaves no doubt as to its constitution, and it was found to be identical with the product derived from 2-*m*-chlorophenoxyphenyldichloroarsine.

With a view to determine the direction of ring closure when substances of type (I) are reduced, it seemed desirable to investigate the simple case where X = CH_3. 3-Methyldiphenylamine-6′-arsinic acid (II) can on ring closure by reduction yield 10-chloro-1-methyl-5 : 10-dihydrophenarsazine (III) and/or 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV).

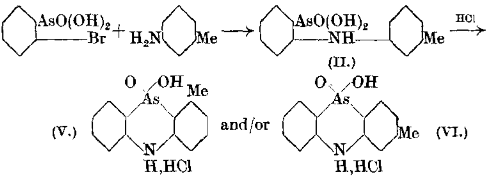


(II.) (III.) (IV.)

The isomeric 2-methyl and 4-methyl homologues (J., 1927, 2508, 2510) of 10-chloro-5 : 10-dihydrophenarsazine have already been synthesised by this method, and in these cases there is no possibility of producing more than one compound in each reaction. In the reaction now under discussion there is no *a priori* reason why either (III) or (IV) should be produced to the complete exclusion of the other, since, whatever the directing influence of the substituted phenylamino-group may be, it is certain to be identical in value for the two ortho-positions in the right hand benzene nucleus of (II), and the effect of the methyl group will be to produce ortho-para-substitution to itself. Presumably the para-directing influence of the methyl group should be stronger than the ortho-, and it seems reasonable to believe that the favoured direction of ring closure will be that leading to the production of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine (IV). Another circumstance which should favour the formation of (IV) by suppressing the formation of (III) is the steric factor, since, as is pointed out in the experimental portion, the difficulty of reducing 3-bromo-*o*-tolylarsinic acid (XII) and the comparative ease with which dearsenication of 3-amino-*o*-tolylarsinic acid (XI) occurs, are separate examples of the protecting action of the adjacent methyl group and bromine atom on the one hand and the reluctance of the arsinic acid group to remain between methyl and amino-groups on the other.

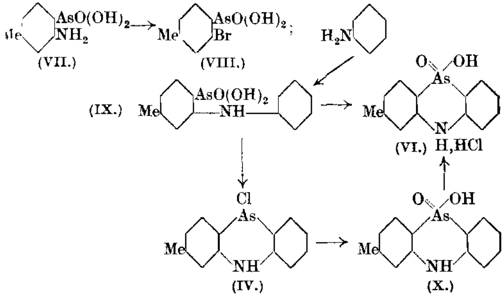
3-*Methyldiphenylamine-6′-arsinic acid* (II) was readily prepared by condensing *o*-bromophenylarsinic acid with *m*-toluidine under

the conditions described in the experimental portion, the crude product being purified through its sodium salt. Ring closure was effected in different ways. On boiling the acid with concentrated hydrochloric acid for a few minutes, the hydrochloride of a methylphenarsazinic acid was produced (compare the hydrochlorides of the 2- and 4-methylphenarsazinic acids, J., 1927, 2508, 2510). The product appeared homogeneous when crystallised from a mixture of ethyl alcohol and concentrated hydrochloric acid, yielding colourless needles, m. p. 232—233° (vigorous decomp.). It may, however, have consisted of the 1-methyl- or the 3-methyl-phenarsazinic acid hydrochloride, or of a mixture of these, formed according to the scheme :



Reduction of 3-methyldiphenylamine-6′-arsinic acid by the alcohol–hydrochloric acid–iodine–sulphur dioxide method gave a yellow product, but although a search for the presence of two substances was carefully carried out, the melting point of the last traces of the crude reduction product separating from the mother-liquor was but slightly lower than that of the main bulk of substance. After repeated recrystallisation from benzene, care being taken to examine all mother-liquors for fractions of differing melting points, the product was obtained in long yellow needles of constant melting point, 216—216·5° : this is a melting point, there being no decomposition as is so often the case with substances of the phenarsazine type. On oxidation with hydrogen peroxide or with chloramine-T, the corresponding methylphenarsazinic acid was obtained in fine colourless needles, decomposing slightly at 316°. Its sodium salt is insoluble in cold concentrated sodium hydroxide solution, and the hydrochloride is indistinguishable from that obtained by boiling 3-methyldiphenylamine-6′-arsinic acid with concentrated hydrochloric acid. On reduction of the methylphenarsazinic acid in hydrobromic acid–alcohol solution, the corresponding methyl-10-bromo-5 : 10-dihydrophenarsazine (m. p. 206—208°) was obtained.

In order to compare the ring compounds derived from 3-methyl-liphenylamine-6′-arsinic acid with substances of known constitu-ion, the synthesis of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine IV) and of 10-chloro-1-methyl-5 : 10-dihydrophenarsazine (III) was .ccomplished in the following manner.

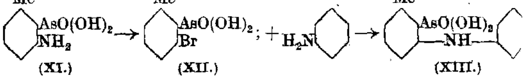


3-Amino-*p*-tolylarsinic acid (VII) (Jacobs, Heidelberger, and Rolf, *J. Amer. Chem. Soc.*, 1918, **40**, 1585) is readily converted into 3-bromo-*p*-tolylarsinic acid (VIII) or the corresponding chloro-ompound by the Sandmeyer reaction. These acids may be con-erted into the corresponding dichloroarsines by reduction, and rom these the corresponding arsenious oxides may be obtained. The acids may also be oxidised to the corresponding 2-bromo-chloro)-4-carboxyphenylarsinic acids by means of an alkaline olution of potassium permanganate. 3-Bromo-*p*-tolylarsinic acid VIII) condensed readily with aniline. The *3-methyldiphenylamine-6-arsinic acid* (IX) produced, purified through its ammonium salt, iad m. p. 158—159° and was quite different, as would be expected rom its mode of preparation, from the isomeric 3-methyldiphenyl-imine-6′-arsinic acid (II). On reduction by the alcohol–hydro-hloric acid–iodine–sulphur dioxide method, this acid gave 10-hloro-3-methyl-5 : 10-dihydrophenarsazine (IV) as a homogeneous product, which crystallised from benzene in yellow needles, m. p. 216—216·5°, and did not depress the melting point of the reduction product of 3-methyldiphenylamine-6′-arsinic acid. On oxidation with hydrogen peroxide or with chloramine-T, 3-methylphenars-azinic acid (X) was obtained, the sodium salt being insoluble in

concentrated sodium hydroxide solution and the hydrochloride having m. p. 231—232° (decomp.). The same hydrochloride was produced on boiling the acid (IX) with concentrated hydrochloric acid, and did not depress the melting point (or rather the decomposition point) of the hydrochloride of the methylphenarsazinic acid formed from (II). Obviously, no stress can be laid on a negative depression of decomposition points, as this may mean anything; on the other hand, if a depression had been produced, it would certainly prove the non-identity of the two substances. 3-Methylphenarsazinic acid on reduction in hydrobromic acid–alcohol solution gave 10-bromo-3-methyl-5 : 10-dihydrophenarsazine, which again was indistinguishable from the bromo-derivative mentioned above.

The evidence thus far indicated that ring closure of (II) gave derivatives of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine and not of the 1-methyl derivative. These indications were, however, found to be untrustworthy, since when the corresponding 1-methyl derivatives were prepared they were only by the very slightest differences, as shown below, distinguishable from the rationally synthesised 3-methyl derivatives.

In describing the method of synthesis of the 1-methyl derivatives, it is necessary to indicate those factors which might have an influence on the product formed when 3-methyldiphenylamine-6′-arsinic acid is subjected to the action of reagents which effect ring closure. The starting point was 3-amino-*o*-tolylarsinic acid (XI) (Jacobs, Heidelberger, and Rolf, *loc. cit.*). This substance is readily dearsenicated by the action of alkalis and acids, *m*-toluidine being formed. The amino-group is readily replaced by bromine or chlorine, yielding *3-bromo(chloro)-o-tolylarsinic acid* (XII). The difficulty of obtaining the *dichloroarsines* by reduction of these acids has been mentioned above, but they were obtained as low-melting solids resembling the isomeric 3-bromo(chloro)-*p*-tolyldichloroarsines in most properties but were less readily attacked by water and alkalis.



(XI.) (XII.) (XIII.)

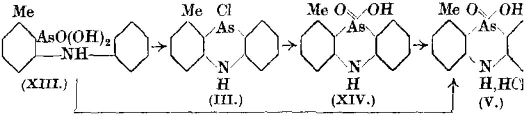
The corresponding *arsenious oxides* were obtained as white amorphous substances by the prolonged action of alkali. These oxides, however, were soluble with difficulty even in a large excess

of hot sodium hydroxide solution. Since the solubility in alkali of phenylarsenious oxides is due to the formation of alkali salts, it is clear that 3-chloro- and 3-bromo-*o*-tolylarsenious oxides have little tendency to salt formation, which is further evidence that the two groups in the two ortho-positions to the arsinic acid group protect it from chemical reaction. When 3-bromo-*o*-tolylarsinic acid was condensed with aniline, *3-methyldiphenylamine-2-arsinic acid* (XIII) was obtained in good yield, in colourless needles, m. p. 170—171° (decomp.).

The three methyldiphenylamine-*o*-arsinic acids are therefore obviously distinct and different from one another. On reduction by the alcohol–hydrochloric acid–iodine–sulphur dioxide method, 3-methyldiphenylamine-2-arsinic acid was *slowly* reduced, so slowly that on one occasion the hydrochloride of the acid (V) separated in almost colourless needles from the cooling solution and, thus escaping reduction, might easily have been mistaken for the reduction product. In order to reduce (XIII) completely it is necessary to heat the liquid, saturated with sulphur dioxide, for some time. This observation bears on the mode of formation of compounds of the phenarsazine type by reduction of diphenylamine-*o*-arsinic acids. The hypothesis has been suggested (J., 1927, 2506) that formation of compounds of the phenarsazine type by reduction of diphenylamine-*o*-arsinic acids takes place through the intermediate formation of the dichloroarsine. It would appear from the results described in the present communication and from the results of investigations which have been made on dimethyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine that the formation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine by reduction of diphenylamine-*o*-arsinic acids may, however, be preceded by the formation of the hydrochloride of the ring-acid, followed by reduction. The previous suggestion would appear then to require some modification, but it may be pointed out that in the reduction of nitromethyldiphenylamine-*o*-arsinic acids (an account of these substances and of the dimethyl and dinitro-derivatives will shortly be submitted for publication) the ring closure must be effected through the dichloroarsine, since they do not form isolable hydrochlorides, nor is ring closure effected by simple boiling with concentrated hydrochloric acid.

The product formed by the reduction of (XIII) must be considered to be *10-chloro-1-methyl-5 : 10-dihydrophenarsazine* (III). It crystallised in yellow needles, m. p. 216—216·5° without decomposition. It did not depress the melting point of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine, nor the melting point of the reduction

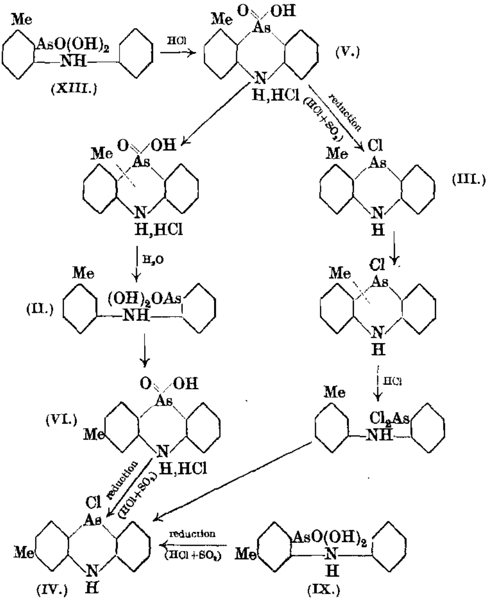
product of (II), several different mixtures being taken. On oxidation, 1-methylphenarsazinic *acid* (XIV) *was obtained, indistinguishable* from the 3-methyl isomeride; its sodium salt was insoluble in cold concentrated sodium hydroxide solution and the hydrochloride (V) had m. p. 231—232° (vigorous decomp.). The hydrochloride of 1-methylphenarsazinic acid was also formed on boiling the acid (XIII) with concentrated hydrochloric acid.



The 1- and 3-methyl derivatives appeared thus to be indistinguishable by the ordinary methods and the problem of deciding whether on ring closure compound (II) gives 1- or 3-methyl derivatives or a mixture of them in any proportions became all the more difficult. Preliminary determinations of the solubilities of methyl-10-chloro-5 : 10-dihydrophenarsazines showed that in benzene, the most suitable solvent, they were apparently equally soluble. Under the microscope they appeared to be the same. Determination of refractive indices or of densities of solutions could not be of much value, since these substances have small solubilities in the suitable solvents at the ordinary and at higher temperatures. An attempt was made to differentiate between the two substances by Sidgwick's freezing-point method (J., 1915, **107**, 672), the solvent being benzene. The solubility at the melting point of benzene was, however, very small and the maximum observed depression of the freezing point of a solution of 10-chloro-1-methyl-5 : 10-dihydrophenarsazine was 0·046° (mean of three determinations). On addition of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine there was a further depression of only 0·004° (mean of two determinations). Therefore no conclusion as to a difference between these two compounds can be drawn from this experiment.

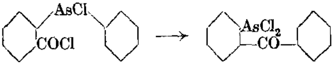
From the evidence which it has been possible to accumulate, it cannot be said that the direction of ring closure in the case of (II) has been ascertained In fact, it is not impossible that 10-chloro-1-methyl-5 : 10-dihydrophenarsazine and 10-chloro-3-methyl-5 : 10-dihydrophenarsazine are one and the same substance. Bearing in mind the ease of dearsenication of 2-amino-6-methylphenarsazinic acid, it will be seen that the formation of 10-chloro-3-methyl-5 : 10-dihydrophenarsazine by reduction of 3-methyldiphenylamine-2-

arsinic acid (XIII) is not impossible according to one of the following schemes :



One observation which would appear to exclude the mechanism indicated on the left is that the hydrochlorides of the ring acids are formed with the greatest ease from the open-chain acids, yet the complete reduction of (XIII) takes place with difficulty, whereas the reduction of (IX) is extremely facile, as indicated in the experimental portion, and the reduction of (II) takes place with intermediate ease as far as can be judged from what can only be qualitative experiments. It may be that this indicates that the reduction product is a mixture of the 1- and 3-methyl isomerides. In this connexion, *a reaction of this type has been discussed by Aeschlimann*

and McCleland (J., 1924, **125**, 2025), who showed that the acid chloride of *o*-carboxydiphenylchloroarsine when heated with aluminium chloride gave benzophenone-*o*-dichloroarsine, thus:



Indications have been obtained of the possibility of determining whether the above two compounds are identical with or different from each other by chemical methods. The accumulation, however, of the necessary materials for the investigation, which requires the carrying out of a very long series of preparations, is very difficult. In the meantime, by the preparation of other derivatives and particularly the examination of other physical properties, including absorption spectra, it is hoped to arrive at a solution of the problem.

EXPERIMENTAL.

If excess of water be avoided in the preparation of 3-amino-*p*-tolylarsinic acid (VII) (Jacobs, Heidelberger, and Rolf, *loc. cit.*), part of the amino-acid is obtained on acidifying the filtrate prior to treatment of the solution with barium chloride. This may be filtered off, and the filtrate treated as described by the above authors except that the concentration of the aqueous solution may be carried out at the ordinary pressure. When crystallised from alcohol, 3-amino-*p*-tolylarsinic acid has m. p. 184—185°.

3-*Chloro*-p-*tolylarsinic acid*, $C_6H_3MeCl\cdot AsO(OH)_2$.—3-Amino-*p*-tolylarsinic acid (10·0 g.), dissolved in hydrochloric acid (18·7 c.c.) and water (16·5 c.c.) by warming, was diazotised below 0° with sodium nitrite (3·33 g.) in water (6·6 c.c.). The diazo-solution was added to a solution of cuprous chloride (3·8 g.) in hydrochloric acid (12·7 c.c.) with constant stirring in the course of about 3 minutes without any cooling. Water (25 c.c.) was added and the liquid stirred for 30 minutes, the precipitated acid then being filtered off, washed with cold water until the washings were colourless, and recrystallised from hot water after treatment with decolorising charcoal. Yield, 7·0 g. (65%).

3-*Chloro*-p-*tolylarsinic acid* forms colourless, flat, truncated prisms, m. p. 189—191° (slight softening at 184°) (Found: Cl, 14·4. $C_7H_8O_3ClAs$ requires Cl, 14·2%). It is almost insoluble in cold water but dissolves fairly readily on boiling; it is readily soluble in concentrated hydrochloric acid, methyl and ethyl alcohols, and alkali hydroxides and carbonates.

3-*Chloro*-p-*tolyldichloroarsine*, $C_6H_3MeCl\cdot AsCl_2$.—The preceding compound (4·3 g.), dissolved in hot concentrated hydrochloric acid

(14 c.c.) containing a trace of iodine, was treated with a rapid stream of sulphur dioxide for about 5 minutes. After cooling, the precipitated oil was extracted with benzene, and the extract filtered from amorphous matter and dried over calcium chloride. The benzene was evaporated and the residual oil was distilled under reduced pressure. The colourless, highly refracting liquid distilled at 166—167°/17 mm. and solidified to a mass of short needles, m. p. 27—29°. The liquid has a marked tendency to supercool (Found : Cl, 39·4. $C_7H_6Cl_3As$ requires Cl, 39·2%). It is readily soluble in ligroin, ethyl alcohol and benzene, but insoluble in water, by which *it is slowly hydrolysed.*

3-*Chloro*-p-*tolylarsenious Oxide*, $C_6H_3MeCl{\cdot}AsO$.—3-Chloro-*p*-tolyldichloroarsine (1·0 g.) was warmed on the water-bath with ammonia solution (*d* 0·88; 5 c.c.) and water (5 c.c.). The pasty mass soon solidified to a white amorphous mass. This was heated for about 20 minutes, collected, well washed with water, dissolved in warm sodium hydroxide solution, and reprecipitated by means of carbon dioxide (distinction from 3-chloro-*p*-tolylarsinic acid). It separated as a white amorphous mass, m. p. 277°. This *oxide* is insoluble in all the usual solvents and in sodium carbonate solution (Found : Cl, 16·6. C_7H_6OClAs requires Cl, 16·4%).

3-*Bromo*-p-*tolylarsinic Acid* (VIII).—The solution prepared by diazotising 3-amino-*p*-tolylarsinic acid (30·0 g.) in hydrobromic acid (*d* 1·265; 100 c.c.) and water (50 c.c.) with sodium nitrite (10·0 g.) in water (20 c.c.) below 0°, was added in the course of about 5 minutes to a solution of cuprous bromide [prepared by mixing solutions of copper sulphate crystals (28·5 g.) in water (94 c.c.) and potassium bromide (14·1 g.) in water (33 c.c.) and saturating the mixture with sulphur dioxide] in hydrobromic acid (*d* 1·49; 51 c.c.) as described for 3-chloro-*p*-tolylarsinic acid, water (60 c.c.) being added afterwards. After 45 minutes' stirring, the orange-coloured precipitate was filtered off and well washed with water. It was recrystallised from hot water after previous treatment with decolorising charcoal and obtained in colourless, flat, truncated prisms, m. p. 208—210° (decomp.). Yield, 72% (Found : Br, 27·4. $C_7H_8O_3BrAs$ requires Br, 27·1%).

The acid is readily soluble in acetic acid, hydrochloric acid, and ethyl alcohol. It is almost insoluble in cold water, and in benzene, but is readily soluble in hot water. A dilute solution of the ammonium salt gave no precipitate with solutions of calcium chloride and barium nitrate. The mercurous salt is a white precipitate soluble in hot water, the silver salt is white and soluble in ammonia, and the mercuric salt forms a brown precipitate somewhat soluble in hot water.

3-*Bromo*-p-*tolyldichloroarsine*, $C_6H_3MeBr{\cdot}AsCl_2$.—A hot solution of the preceding compound (8·3 g.) in hydrochloric acid (25 c.c.) containing a trace of iodine was reduced with sulphur dioxide. The oily product was worked up as described for 3-chloro-*p*-tolyldichloroarsine. 3-*Bromo*-p-*tolyldichloroarsine* was thus obtained in 60% yield as a colourless, highly refracting liquid, b. p. 176—177°/14 mm., which solidified to a mass of radiating needles, m. p. 47—49° (Found: 0·3059 g. gave 0·4632 g. of mixed silver halides. $C_7H_6Cl_2BrAs$ requires 0·4596 g.). It is soluble in ligroin and benzene and only slowly attacked by water, in which it is insoluble.

3-*Bromo*-p-*tolylarsenious oxide*, $C_6H_3MeBr{\cdot}AsO$, was obtained by treating the preceding compound (2·94 g.) with ammonia (10 c.c.) and water (10 c.c.) as described for the chloro-compound. It was obtained as a white amorphous mass, m. p. 266—268°, insoluble in the ordinary organic solvents but soluble in caustic alkalis, from which solutions it was precipitated by carbon dioxide (Found: Br, 30·9. C_7H_6OBrAs requires Br, 30·7%).

2-*Chloro*-4-*carboxyphenylarsinic Acid*, $CO_2H{\cdot}C_6H_3Cl{\cdot}AsO(OH)_2$.—A warm solution of 3-chloro-*p*-tolylarsinic acid (5·0 g.) in sodium carbonate (decahydrate, 5·7 g., in water, 20 c.c.) was added to potassium permanganate (12·6 g.) in water (312 c.c.) and boiled during 8 hours. A current of carbon dioxide was continually passed through the mixture in order to minimise the replacement of the chlorine by hydroxyl by means of the potassium hydroxide formed during the oxidation. The resulting solution was filtered whilst hot, and the manganese dioxide extracted with boiling water. The aqueous solutions were mixed and concentrated to about 250 c.c., cooled, and acidified with concentrated hydrochloric acid. 2-*Chloro*-4-*carboxyphenylarsinic acid* was slowly precipitated as colourless needles or long flat plates, unmelted at 310° (Found: Cl, 12·6. $C_7H_6O_5ClAs$ requires Cl, 12·65%). The alkali salts are readily soluble in water; the barium salt forms rhomb-shaped plates, the calcium salt tufts of colourless needles; the silver, mercurous and mercuric salts are white precipitates, the first being soluble in ammonia. The magnesium salt appears to be soluble in water and not precipitated under ordinary conditions.

2-*Bromo*-4-*carboxyphenylarsinic Acid*, $CO_2H{\cdot}C_6H_3Br{\cdot}AsO(OH)_2$.—The oxidation of 3-bromo-*p*-tolylarsinic acid (9·45 g.) in sodium carbonate (decahydrate, 9·15 g., in water, 30 c.c.) with potassium permanganate (20·24 g.) in water (500 c.c.) was carried out as for the preceding substance. The product (yield, 65%) formed colourless needles, unmelted at 317°, slightly soluble in boiling water, almost insoluble in the cold (Found: Br, 24·8. $C_7H_6O_5BrAs$ requires Br, 24·6%).

3-Methyldiphenylamine-6-arsinic Acid (IX).—A mixture of 3-bromo-*p*-tolylarsinic acid (11·8 g.), aniline (3·75 g.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (35 c.c.), and a trace of copper powder was boiled for 5 hours. Volatile substances were removed from the product by steam distillation and the filtered aqueous solution after treatment with decolorising charcoal was carefully acidified with dilute hydrochloric acid. A discoloured pasty mass (7·55 g., 63%) was precipitated. It was filtered off, well washed with water, and dried in a desiccator. The acid so obtained is sufficiently pure for most of the preparations described below, but the crude acid, which cannot be conveniently crystallised, was purified as follows. It was thoroughly mixed with a little concentrated solution of ammonia in the cold, and the mixture cautiously warmed to bring about solution; concentrated ammonia solution was then added and, if care had been taken to avoid loss of ammonia by excessive heating, the solution on cooling and stirring deposited the ammonium salt in clusters of colourless needles. The ammonium salt was filtered off and dissolved in water, and the solution acidified with dilute hydrochloric acid. The precipitated acid was dissolved in boiling 50% acetic acid and water added until the solution became slightly turbid; the liquid was heated to boiling, treated with decolorising charcoal and filtered; the filtrate on cooling deposited *3-methyldiphenylamine-6-arsinic acid* in colourless needles, m. p. 158—159° (turning slightly brown) (Found: As, 24·5. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). The acid is readily soluble in acetic acid, methyl and ethyl alcohols and acetone. Its solubility in water is very small. The sodium, potassium and ammonium salts are readily soluble in water, the silver, lead and mercuric salts form white flocculent precipitates insoluble in cold and hot water; the silver salt is soluble in ammonia. The mercurous, calcium, and barium salts are white precipitates insoluble in cold but soluble in hot water. The magnesium salt is formed only when a solution of the ammonium salt is boiled with magnesia mixture.

10-Chloro-3-methyl-5 : 10-dihydrophenarsazine (IV).—3-Methyldiphenylamine-6-arsinic acid (crude or pure, 3·45 g.), dissolved in a hot mixture of hydrochloric acid (15 c.c.) and alcohol (15 c.c.) containing a trace of iodine, was reduced by passing sulphur dioxide for a few minutes. Reduction and ring closure took place immediately, solid matter separating as soon as sulphur dioxide passed through the liquid. After cooling, the precipitated solid (2·2 g.) was filtered off, washed with a little alcohol, and dried at 100°. It was recrystallised from benzene and obtained in slender yellow needles, m. p. 216—216·5° (Found: Cl, 12·2. $C_{13}H_{11}NClAs$

requires Cl, 12·1%). It is sparingly soluble in benzene at the ordinary temperature but more soluble in the hot solvent; it is somewhat readily soluble in acetone.

3-*Methylphenarsazinic Acid* (X).—(*a*) 10-Chloro-3-methyl-5 : 10-dihydrophenarsazine (2·0 g.), dissolved in cold acetone (70 c.c.), was treated with a cold solution of chloramine-T (4·5 g.) in water (63 c.c.). The yellow colour of the chloro-compound immediately disappeared and in a few minutes colourless crystalline material (1·6 g., 81%) began to separate. After 30 minutes, this was filtered off, well washed with water, and crystallised from glacial acetic acid, in which it was moderately easily soluble on boiling. The compound was obtained in clusters of fine colourless needles which retained a molecule of acetic acid of crystallisation even after drying over potassium hydroxide (Found : $C_2H_4O_2$, 17·2; As, in "dry" material, 25·55. $C_{13}H_{12}O_2NAs,C_2H_4O_2$ requires $C_2H_4O_2$, 17·2%. $C_{13}H_{12}O_2NAs$ requires As, 25·95%). The compound decomposes slightly at 316°.

(*b*) 10-*Chloro-3-methyl-5 : 10-dihydrophenarsazine* (2·0 g.) was boiled in acetic acid suspension (20 c.c.) with hydrogen peroxide (20 vols., 4·0 c.c.). The yellow chloro-compound was rapidly replaced by a white solid. After a few minutes' boiling, the liquid was cooled, water (80 c.c.) added, and the solid material filtered off and well washed with water. It was dissolved in hot dilute sodium hydroxide solution and treated with decolorising charcoal, and to the hot filtrate 25% sodium hydroxide solution was added in excess. On cooling, the sodium salt crystallised in fine colourless needles. This was filtered off and dissolved in warm water, and the acid (1·6 g., 79%) precipitated with concentrated hydrochloric acid. The acid, after drying at 150°, appeared to be identical with the product obtained by the previous method.

The *hydrochloride* (VI) of 3-methylphenarsazinic acid was prepared in two ways. (*a*) A solution of 3-methylphenarsazinic acid (1·6 g.) in a hot mixture of alcohol (47 c.c.) and hydrochloric acid (14 c.c.) was allowed to cool. The hydrochloride was deposited in fine colourless needles or elongated plates, m. p. 232—233° (decomp., turning emerald-green) (Found : Cl, 11·2. $C_{13}H_{12}O_2NAs,HCl$ requires Cl, 10·9%). What appeared to be the same hydrochloride was obtained whether the 3-methylphenarsazinic acid had been prepared by method (*a*) or (*b*) described above.

(*b*) 3-Methyldiphenylamine-6-arsinic acid was boiled with an excess of concentrated hydrochloric acid; it liquefied, emitting the characteristic odour which has been mentioned previously (J., 1927, 2503), and within half a minute crystalline material began to separate. After cooling, this was filtered off and recrystallised from

a mixture of alcohol and hydrochloric acid. It appeared to be identical with the product obtained by method (*a*).

10-*Bromo-3-methyl-5 : 10-dihydrophenarsazine* (formula as IV).—3-Methylphenarsazinic acid (0·82 g.) was dissolved in a boiling mixture of hydrobromic acid (*d* 1·49; 12 c.c.) and alcohol (12 c.c.) containing a trace of iodine and reduced by passage of sulphur dioxide for a few minutes. After cooling, the precipitated *bromo-compound* (0·77 g.) was filtered off, washed with alcohol, and dried at 150°. It was recrystallised from benzene and obtained in orange rectangular plates or slender needles, m. p. 206—208° (Found: Br, 24·1. $C_{13}H_{11}NBrAs$ requires Br, 23·8%).

3-*Nitro*-p-*tolyldichloroarsine*, $NO_2{\cdot}C_6H_3Me{\cdot}AsCl_2$.—3-Nitro-*p*-tolylarsinic acid (2·85 g.), dissolved in boiling hydrochloric acid (20 c.c.) containing a little hydriodic acid, was saturated with sulphur dioxide. The precipitated oil soon solidified and after drying on porous porcelain it was crystallised from ligroin (b. p. 60—80°). The compound obtained formed pale yellow, flat prisms, m. p. 113° (Found: Cl, 25·0. $C_7H_6O_2NCl_2As$ requires Cl, 25·2%).

3-Nitro-*o*-toluidine (Gabriel and Thieme, *Ber.*, 1919, **52**, 1079) was converted into 3-nitro-*o*-tolylarsinic acid by the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*). After coupling of the diazo-solution as described with alkaline sodium arsenite solution, precipitation of feebly acidic substances with acetic acid, and treatment with charcoal, the cooled filtrate on acidification with hydrochloric acid should yield the nitro-arsinic acid, m. p. 223—230° (decomp.). It was found that if an excess of acetic acid was added to the "coupled" solution in the first place, the cooled filtrate deposited colourless needles before the addition of hydrochloric acid. The precipitated substance could be recrystallised from water, was soluble in sodium carbonate, sodium hydroxide or ammonia solution, and was reprecipitated on addition of acetic acid. The air-dried material melted at 97°, resolidified at 125—130°, and then remained unmelted at 300°. When the substance in sodium hydroxide solution was acidified with hydrochloric, hydrobromic or sulphuric acid, the nitro-arsinic acid, m. p. 228—230°, was obtained. This, dissolved in sodium hydroxide solution, gave the substance, m. p. 97° (etc.), on acidification with acetic acid. This substance proved to be the *sodium hydrogen* salt of 3-nitro-*o*-tolylarsinic acid and it is formed whenever a solution of the acid in sodium hydroxide is acidified with acetic acid, whereas mineral acids precipitate the nitro-acid itself [Found in air-dried material: As, 19·3; N, 3·8; Na, 5·9; H_2O (over phosphoric oxide), 26·9 (by heating, slight decomposition), 29·5. $C_7H_7O_5NAsNa,6H_2O$ requires As, 19·2; N, 3·6; Na, 5·9; H_2O, 27·6%]. 3-Nitro-*o*-tolylarsinic acid is colourless.

3-*Nitro*-o-*tolyldichloroarsine*, $NO_2{\cdot}C_6H_3Me{\cdot}AsCl_2$.—A boiling solution of 3-nitro-*o*-tolylarsinic acid (12 g.) in hydrochloric acid (60 c.c.) containing a trace of iodine was reduced by passage of sulphur dioxide for a few minutes. An oil was precipitated which solidified on cooling; it was filtered off, washed with concentrated hydrochloric acid, pressed on porous porcelain, and crystallised from ligroin (b. p. 60—80°, decolorising charcoal being used). The *compound* (7·0 g.) separated in pale yellow needles, m. p. 93° (Found : Cl, 24·9. $C_7H_6O_2NCl_2As$ requires Cl, 25·2%). It is readily soluble in acetone and benzene and somewhat less soluble in ligroin. Like other dichloroarsines, it is hydrolysed by water.

3-*Nitro*-o-*tolyldibromoarsine*, $NO_2{\cdot}C_6H_3Me{\cdot}AsBr_2$.—On boiling 3-nitro-*o*-tolylarsinic acid (12·2 g.) with hydrobromic acid (*d* 1·49; 100 c.c.) containing a trace of iodine, bromine was evolved and an oil separated, the hydrobromic acid apparently acting as a reducing agent. Reduction was completed by saturating the solution with sulphur dioxide, and the product worked up as in the previous preparation. Recrystallised from benzene–ligroin (b. p. 60—80°), the *dibromoarsine* (16 g., 92%) was obtained in pale yellow, flat plates, m. p. 116·5—117·5° (Found : Br, 42·8. $C_7H_6O_2NBr_2As$ requires Br, 43·1%).

3-Amino-*o*-tolylarsinic acid (XI) was prepared according to the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*). Contrary to the case of 3-amino-*p*-tolylarsinic acid (p. 776), the evaporation of the aqueous solution of the sodium salt must be carried out under reduced pressure, otherwise considerable dearsenication occurs and the yield is very small. Even when the evaporation was carried out under reduced pressure the aqueous distillate contained *m*-toluidine (formed by dearsenication), which was identified by conversion into 2 : 4 : 6-tribromo-*m*-toluidine (m. p. 97°). After the solution had been concentrated it was cautiously acidified and the amino-acid mixed with a little salt, was filtered off, roughly dried, and boiled with alcohol to separate the amino-acid from the salt. The alcoholic filtrate on concentration deposited the pure amino-acid. The alcoholic mother-liquor on further evaporation left a dark-coloured oil, which solidified on the addition of water. This product was recrystallised from hot water (decolorising charcoal) and was then obtained in pale pink needles, m. p. 117°, unchanged on further recrystallisation. On treatment with dilute sodium hydroxide solution, this substance gave an oil which was identified as *m*-toluidine (benzoyl derivative, m. p. 125°). The properties of the substance indicated that it was a salt of *m*-toluidine and it was therefore compared with the *arsenate* of *m*-toluidine. This was prepared by adding *m*-toluidine (10 g.) to a hot solution of arsen

acid (14 g.) in water (56 c.c.), treating it with decolorising charcoal, and filtering and cooling it. *m*-Toluidine arsenate crystallised in colourless leaflets, softening at 93° and melting at 141—144° (Found: N, 5·8; As, 30·4. C_7H_9N,H_3AsO_4 requires N, 5·6; As, 30·2%). The substance obtained as a by-product in the above preparation was not identical with *m*-toluidine arsenate, and its nature is for the present unknown.

3-*Chloro*-o-*tolylarsinic Acid*, $C_6H_3MeCl{\cdot}AsO(OH)_2$.—3-Amino-*o*-tolylarsinic acid (12·0 g.) was dissolved in a mixture of hydrochloric acid (22·4 c.c.) and water (20 c.c.) and diazotised below 5° with a solution of sodium nitrite (4·0 g.) in water (8·0 c.c.). Towards the end of the diazotisation the diazo-compound separated in pale yellow needles; separation of the diazo-compound also took place during the preparation of the corresponding bromo-compound (below). The suspension was added at the ordinary temperature with constant stirring to a solution of cuprous chloride (4·55 g.) in hydrochloric acid (15·3 c.c.), ether being used to control excessive frothing. The mixture was heated on the water-bath to complete the reaction, water added, and the *chloro-acid* (9·85 g., 76%) filtered off, well washed with water, and crystallised from alcohol. It was obtained in colourless prisms or prismatic needles, m. p. 236—239° (decomp.) after slight softening at 232° (Found: Cl, 13·9. $C_7H_8O_3ClAs$ requires Cl, 14·2%). It is readily soluble in ethyl alcohol and in acetic acid, but almost insoluble in water. The silver and mercurous salts are characteristic: the former is precipitated in clusters of colourless needles and the latter in fine colourless needles.

3-*Chloro*-o-*tolyldichloroarsine*, $C_6H_3MeCl{\cdot}AsCl_2$.—The preceding compound (7·5 g.) was dissolved in boiling hydrochloric acid (20 c.c.) containing a little hydriodic acid, and the solution saturated with sulphur dioxide. Reduction was very slow, it being necessary to boil the solution several times during the reduction to prevent the precipitation of the acid. This retardation of reduction clearly indicates steric hindrance and was even more marked in the case of the reduction of 3-bromo-*o*-tolylarsinic acid (see below). The crude product was a thick oil, which was worked up as described for the isomeric 3-chloro-*p*-tolyldichloroarsine. It distilled at 156°/11 mm. as a colourless oil, rapidly assuming a pink colour. It has m. p. 37·5° and forms colourless stout prisms (yield, 78%) (Found: Cl, 39·4. $C_7H_6Cl_3As$ requires Cl, 39·2%). It has a phenolic odour and is readily soluble in the ordinary organic solvents. It is slowly hydrolysed by water, forming the oxide.

3-*Chloro*-o-*tolylarsenious Oxide*, $C_6H_3MeCl{\cdot}AsO$.—The preceding substance (1·75 g.) was heated with water (10 c.c.) and ammonia

(10 c.c.) on the water-bath. The conversion of the dichloroarsine into the arsenious oxide was hindered by the latter forming an insoluble protecting coating over the former; benzene was therefore added and the mixture well shaken at intervals during the heating (1 hour) on the water-bath. The colourless *3-chloro-o-tolylarsenious oxide*, being insoluble in water and all the usual organic solvents, was filtered off and thoroughly washed. It is insoluble in alkali carbonate and hydroxide solutions. At 234—237° it forms a milky liquid, clearing at 254° (Found: Cl, 16·15. C_7H_6OClAs requires Cl, 16·4%).

3-Bromo-o-tolylarsinic Acid (XII).—This substance was obtained in 75% yield in a manner similar to that used for the isomeric compound (p. 777), except that the evolution of nitrogen after mixture of the diazo-solution with the copper solution was completed by heating on the water-bath for 30 minutes instead of by stirring the liquid for 45 minutes. The product crystallised from aqueous alcohol in colourless thin needles. At 200°, it shrank somewhat; at 245°, it appeared to be converted into a white powder which remained unmelted at 306°. When the melting-point tube was introduced into the preheated apparatus at 260°, the substance melted to a clear liquid, effervesced, and then solidified to a white powder which remained unmelted at 306°. It is suggested that these phenomena indicate the formation of an anhydride which remains unmelted at 306° (Found: Br, 27·2. $C_7H_8O_3BrAs$ requires Br, 27·1%). The *acid* resembles the corresponding chloro-acid in general properties. The alkali and mercuric salts appear to be readily soluble in water; the silver, lead, and mercurous salts are white curdy precipitates; the magnesium salt is formed as a white amorphous precipitate only on boiling a strong solution of the ammonium salt with magnesia mixture; the calcium salt forms colourless needles, and the barium salt colourless plates, only when a strong solution of the ammonium salt is boiled with solutions of the appropriate metallic salts.

3-Bromo-o-tolyldichloroarsine, $C_6H_3MeBr{\cdot}AsCl_2$.—A boiling solution of 3-bromo-*o*-tolylarsinic acid (10·0 g.) in a mixture of hydrochloric acid (16·0 c.c.) and alcohol (10 c.c.) containing a little hydriodic acid was reduced, and the product worked up as described for 3-chloro-*o*-tolyldichloroarsine. It distilled as an almost colourless oil, b. p. 170—171°/13 mm., which solidified in a freezing mixture to a mass of stout prisms, m. p. 25—27° (Found: 0·6464 g. gave 0·9693 g. of mixed silver halides. $C_7H_6Cl_2BrAs$ requires 0·9712 g.) (yield, 6·8 g.). The compound had a faint, not unpleasant odour; it was soluble in all the usual organic solvents and was slowly hydrolysed by water.

3-Bromo-o-tolylarsenious Oxide, $C_6H_3MeBr{\cdot}AsO$.—The preceding substance (1·25 g.) was heated with water (5 c.c.) and ammonia (5 c.c.) on the water-bath, the conversion into the colourless *oxide* being very slow. The product was insoluble in the usual organic solvents and in alkali carbonates, but it dissolved slightly in a large volume of sodium hydroxide solution, from which it was reprecipitated in an amorphous condition by passage of carbon dioxide. It had an indefinite melting point, 214—219° (Found: Br, 30·7. C_7H_6OBrAs requires Br, 30·7%).

3-Methyldiphenylamine-2-arsinic Acid (XIII).—A mixture of 3-bromo-*o*-tolylarsinic acid (11·8 g.), aniline (3·75 g.), anhydrous potassium carbonate (8·8 g.), amyl alcohol (35 c.c.), and a trace of copper powder was boiled for 5 hours. Volatile substances were removed by steam distillation and the aqueous solution was treated with decolorising charcoal, cooled, and carefully acidified with dilute hydrochloric acid. The precipitated *acid* (8·2 g., 67%) was almost colourless. It was recrystallised from dilute acetic acid (50%) and obtained in colourless needles, m. p. 170—171° (decomp.) (Found: As, 24·3. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). The acid is soluble in alcohol and acetic acid and almost insoluble in water. The sodium salt is precipitated on cooling its solution in 20% sodium hydroxide solution; the silver, lead, mercurous, and mercuric salts are white amorphous precipitates; the ammonium, calcium and magnesium salts appear to be readily soluble in water; the barium salt crystallises from hot water in colourless plates.

10-Chloro-1-methyl-5:10-dihydrophenarsazine (III).—The preceding acid (5·5 g.), dissolved in a boiling mixture of alcohol (40 c.c.) and hydrochloric acid (40 c.c.) containing a trace of iodine, was reduced by passing a current of sulphur dioxide for some time. Reduction does not take place so readily as with the two isomeric acids (II) and (IX), it being necessary to boil the solution repeatedly during the reduction and to heat it on the water-bath for 30 minutes afterwards to complete the reaction. (The hydrochloride of the ring-acid tends to separate if the solution cools during the reduction and this is not very readily attacked.) The crystalline product was dried in a desiccator over potassium hydroxide and recrystallised from glacial acetic acid (the crystals retaining some green colouring matter) and then twice from benzene. It was obtained in slender, prismatic, yellow needles, m. p. 216—216·5° (Found: Cl, 11·8. $C_{13}H_{11}NClAs$ requires Cl, 12·1%). It dissolves fairly readily in acetone.

1-Methylphenarsazinic Acid (XIV).—The oxidation of the preceding compound was carried out as described for the 3-methyl isomeride (p. 780). The product crystallised from acetic acid

in colourless needles, m. p. 316° (decomp.) (Found: As, 25·7. $C_{13}H_{12}O_2NAs$ requires As, 25·95%). The most characteristic salt is the sodium salt, which crystallises from a 20% sodium hydroxide solution in fine colourless needles.

1-*Methylphenarsazinic acid hydrochloride* (V) was prepared in two ways:

(*a*) 3-Methyldiphenylamine-2-arsinic acid (1·1 g.) was boiled for a few minutes with concentrated hydrochloric acid (8 c.c.) and when the oil first formed had been replaced by a crystalline precipitate (about 1 minute), alcohol (8 c.c.) was added, the solution then being quite clear while boiling. On cooling, the *hydrochloride* separated in fine needles, m. p. 231—232° (decomp., turning emerald-green) (Found: Cl, 10·8. $C_{13}H_{12}O_2NAs,HCl$ requires Cl, 10·9%).

(*b*) A solution of 1-methylphenarsazinic acid (1·0 g.) in a boiling mixture of alcohol (25 c.c.) and hydrochloric acid (8 c.c.) was allowed to cool. The product appeared to be identical with that prepared by method (*a*).

3-*Methyldiphenylamine-6′-arsinic Acid* (II).—A mixture of *o*-bromophenylarsinic acid (21·0 g.), *m*-toluidine (8·0 g.), amyl alcohol (65 c.c.), anhydrous potassium carbonate (16·3 g.), and a trace of copper powder was boiled for 5 hours, and the product worked up in the manner already described for the isomeric compounds. It was purified through the sodium salt. The crude acid (14 g., 61%) was dissolved in hot 10% sodium hydroxide solution and to the boiling filtered solution, 25% sodium hydroxide solution was added until the crystalline sodium salt began to separate. After cooling, this was filtered off and worked up in the manner described for the ammonium salt of 3-methyldiphenylamine-6-arsinic acid The *acid* was obtained from its solution in dilute acetic acid in clusters of prismatic needles or elongated hexagonal prisms, m. p. 141—142° after slight softening (Found: As, 24·6. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). It is readily soluble in acetic acid and in ethyl alcohol, but insoluble in water.

Reduction of 3-Methyldiphenylamine-6′-arsinic Acid.—The preceding compound (crude or pure, 14·0 g.), dissolved in a hot mixture of hydrochloric acid (80 c.c.) and alcohol (80 c.c.) containing a trace of iodine, was reduced and the product worked up as described for 10-chloro-3-methyl-5 : 10-dihydrophenarsazine. The main portion of the crude product had m. p. 210—213° and the last portion separating from the mother-liquor had m. p. 209—210°. After one recrystallisation from benzene, the product (A) had m. p. 216—217° and this was unchanged by further recrystallisation (Found: Cl, 12·3. $C_{13}H_{11}NClAs$ requires Cl, 12·1%).

Oxidation of the 1- *and/or* 3-*Methyl*-10-*chloro*-5 : 10-*dihydrophenarsazine.*—The preceding substance was oxidised by both methods described for the preparation of 3-methylphenarsazinic acid, the product being indistinguishable from the rationally synthesised 1-methyl- and 3-methyl-phenarsazinic acids. The sodium salt, colourless needles, was also insoluble in a cold concentrated solution of sodium hydroxide.

Effects of Acids on 3-*Methyldiphenylamine*-6′-*arsinic Acid.*—On boiling 3-methyldiphenylamine-6′-arsinic acid with concentrated hydrochloric acid the same phenomena as were observed in the case of 3-methyldiphenylamine-6-arsinic acid and 3-methyldiphenylamine-2-arsinic acid were noticed. The hydrochloride isolated crystallised from alcohol–hydrochloric acid in fine colourless needles having m. p. 232—233° (vigorous decomp., turning emerald-green), indistinguishable from the hydrochloride of either 1-methyl- or 3-methylphenarsazinic acid. On boiling 3-methyldiphenylamine-6′-arsinic acid with 50% sulphuric acid for a few minutes and cooling and diluting the solution, what appeared to be 3-methylphenarsazinic acid was precipitated.

1- *and/or* 3-*Methyl*-10-*bromo*-5 : 10-*dihydrophenarsazine.*—The reduction of 1- and/or 3-methylphenarsazinic acid to give 1- and/or 3-methyl-10-bromo-5 : 10-dihydrophenarsazine was carried out as described for the 3-methyl compound. The products appeared to be identical when compared under the microscope and no depression of melting point of the mixed substances was observed.

Comparison of the Reduction Product (*A*) *of* 3-*Methyldiphenylamine*-6′-*arsinic Acid with the Rationally Synthesised* 10-*Chloro*-1-*methyl- and* -3-*methyl*-5 : 10-*dihydrophenarsazines.*—Mixed melting-point determinations on mixtures of 10-chloro-1- and -3-methyl-5 : 10-dihydrophenarsazines, which both melt at 216—217°, failed to show any depression. As a natural consequence of this remarkable fact, it was observed that mixtures of product (A) and these two substances separately also showed no depression of the melting point. From this it followed that product (A) could be the pure 1-methyl compound, the pure 3-methyl compound, or any possible mixture of 10-chloro-1-methyl- and -3-methyl-5 : 10-dihydrophenarsazines.

The solubilities of 10-chloro-1-methyl- and -3-methyl-5 : 10-dihydrophenarsazines in benzene were found to be approximately the same, *viz.*, about 0·3% at the ordinary temperature and about 3% at the boiling point.

Guy's Hospital Medical School (University of London),
London, S.E. 1. [*Received, February 25th,* 1929.]

CIX.—*The Apparent Influence of an Electric Field on the Boiling Point of Benzene.*

By John William Smith.

It has been shown by Baker (J., 1928, 1051) that if benzene is introduced into tubes containing two parallel platinum plates, which are connected to a 400-volt battery for some hours, the boiling point of the benzene is raised from 80° to 91°; and similar changes are observed in surface tension. These changes were attributed to changes in the internal complexity of the benzene owing to the moisture being unable to form into droplets, which were supposed, on Sir J. J. Thomson's theory (*Phil. Mag.*, 1893, **36**, 320), to cause the so-called normal behaviour of the liquid. Subsequently, Smits (J., 1928, 2399) found that, although the apparent boiling point was raised considerably when the tube was heated in an oil bath, the liquid still boiled at the normal temperature when the tube was heated directly with a small flame, and that the vapour pressure was unchanged; hence he concluded that Baker's high boiling points were due to superheating, which is induced by the removal of electrically charged dust particles by the electric field, and is facilitated when heating is carried out in a bath. The removal of dust particles was also supposed to account for the abnormalities in surface tension.

Although the experiments now described confirm those of Smits, several other observations have been made which are considered worthy of record.

Experimental.

The benzene used was Kahlbaum's "thiophene-frei," and contained no detectable amount of thiophen. After being frozen out twice, it was distilled, and the middle fraction was stored over phosphoric oxide for a few days and distilled from this reagent before use.

Baker's simple experiment was first repeated, the benzene being sealed into a tube containing two parallel electrodes of platinum foil and two thermometers, one suspended in the liquid and the other in the vapour. The top of the tube was drawn out to a long capillary of about 2 mm. diameter, which was bent twice at right angles After the tube was charged with the benzene, the end of this capillary tube was sealed, and a *P.D.* of 540 volts applied to the electrodes. After a week the capillary tube was opened under dry mercury, and the bulb immersed in an oil bath, the temperature of which was raised gradually. At about 80°, considerable evaporation occurred from the benzene, as shown by refluxing down the walls of the vessel, but no visible ebullition occurred. At 84·5°

bubbles began to rise from the electrodes, but the thermometer in the vapour registered 80°. One of the leads then accidentally became dislodged, whereupon boiling instantly ceased, but resumed as soon as the lead was restored. Hence the leads were removed and the heating continued. The temperature rose to 85·5° before ebullition recommenced. The temperature of the liquid fluctuated between 85° and 86°, but the thermometer in the vapour remained at 80°. If the leads were restored whilst gentle ebullition was occurring at 85·5°, the liquid boiled much more violently, the temperature falling to 84·5°, but became quiescent again as soon as they were removed.

Another specimen in a similar tube boiled at 87°, and continued at that temperature while most of the benzene was boiled away. When only a little was left, however, the temperature rose to 93°. The highest temperature recorded in the vapour was 81°, but, as this was reached when only very little liquid remained, it was probably due to some superheating of the vapour.

An experiment was carried out in the same tube under similar conditions with benzene which had not been subjected to the electric field. The boiling point as registered by the thermometer in the liquid was 80·5°, and that in the vapour 80°. When only a very small amount of liquid remained, the temperature in the liquid rose to 81°, but the vapour temperature was still 80°. In this case, however, the temperature of the bath was only slightly higher than that of the liquid in the tube, whereas in the case of the benzene which had been under the electric field the bath had to be taken to a much higher temperature (105°) in order to cause ebullition. It has been observed throughout these experiments that after a temperature of about 80° was passed, the temperature of the liquid in the bulb remained always considerably below that of the bath, although comparatively thin-walled glass tubes were employed. This is attributed to the rapid evaporation from the surface of the liquid, and the return of condensed liquid into the bulb. In many cases this effect made it difficult to raise the temperature of the benzene sufficiently to cause it to boil visibly.

A series of experiments was also carried out in order to test whether any change in vapour pressure occurred on subjecting the liquid to an electric field. Both mercury and glass-spring indicator gauges were employed, but the results were entirely negative, although electric fields up to about 1500 volts per cm. were applied and the temperature of measurement was varied from 0° to 80°. Boiling-point observations showed that the presence of mercury was detrimental to the production of the phenomenon, and also that less effect was observed when there was a considerable "dead

space" not under the electric field at the side of and behind the electrodes.

In one apparatus in which a glass-spring indicator was employed, a *P.D.* of 440 volts was applied to electrodes 1 cm. apart in the benzene for a month without causing any change in vapour pressure. A side bulb was then immersed in ice, and after about one-third of the liquid had condensed in it, the bulb was sealed off, a fraction of the liquid being thus removed. The rate of attainment of the previous vapour pressure, however, was almost exactly the same as when a fraction was removed under similar conditions before application of the field. This behaviour contrasts strongly with that of intensively dried liquids, in which the rate of attainment of a constant vaponr pressure is extremely slow.

In order to avoid the presence of any "dead space," another type of cell was employed. A flat bulb was constructed with parallel sides, about 7 mm. apart, platinum wires being sealed through each face. In order to form two parallel silver plates on these walls, paraffin wax was run round the edge of the bulb, so as to form a thin but continuous layer. The interior of the bulb was then silvered. The paraffin wax was removed by repeated washing with benzene. Thus the silver deposits on the two faces remained effectively insulated from one another. Again, with this type of vessel, no vapour-pressure change could be detected after connecting the electrodes to a *P.D.* of 400 volts for a month. Boiling-point determinations with such a cell furnished some interesting results, however, which serve to throw some light on the cause of the high apparent boiling point.

A small thermometer was suspended in the liquid by means of a platinum wire, so that its bulb was equidistant from the faces and approximately in the centre of the liquid. Without the top of the tube being sealed, a *P.D.* of only 220 volts was applied to the electrodes, but after two or three days the apparent boiling point was raised considerably. The heating was carried out by means of an oil bath, and on some occasions the temperature of the liquid in the bulb could be raised to 104° before ebullition commenced. This occurred suddenly, and the temperature fell a few degrees, after which the liquid boiled steadily at 96°. As has been found in all these experiments, the bubbles arose from one point on one of the electrodes, in this case from one of the platinum wires sealed through the wall of the vessel. If, however, whilst the temperature was about 90°, the liquid was stirred vigorously with the thermometer, bubbles escaped violently from the liquid in the tube, and the temperature fell. As soon as agitation was discontinued, however, the ebullition ceased, and the temperature began to rise again.

The more vigorously the liquid was stirred, the lower the temperature became. In this way it was possible to lower the temperature of the liquid from 94° to 82°. The actual temperature at which the unagitated liquid boiled was by no means reproducible. After the electric field had been applied for a day, the boiling point did not appear to rise progressively with time, but, in general, the unagitated liquid attained steady boiling at some temperature between 90° and 100°, and this ebullition showed none of the characteristics of superheating as generally observed. When the liquid to which the field had not been applied was kept boiling gently at 80·5°, no rise in this boiling point could be observed when the field was applied for four hours. Thus it would appear that the agitation caused by the boiling destroyed the effect which the electric field tends to produce.

The boiling point found when the bulb was heated directly with a small flame was in complete accordance with the observations of Smits (*loc. cit.*), for it was always unaltered whatever the duration of the electric field, and even with specimens of benzene which boiled steadily at temperatures as high as 96° when heated in an oil bath.

Hence it appears certain that Baker's observation of a rise in boiling point after application of an electric field was due, as suggested by Smits, to superheating induced by the removal of charged nuclei from the system.

Summary.

When an electric field is applied to benzene in a tube heated by means of an oil bath, the apparent boiling point, as registered by a thermometer in the liquid, rises, as has been shown by Baker. The vapour temperature, however, retains its normal value. This effect is not observed when the tube is heated directly with a small flame. The effect is considerably reduced by stirring, and the more so the more vigorous the agitation. No change in vapour pressure occurs when benzene is subjected to an electric field. The effect observed by Baker is attributed to superheating.

In conclusion, the author desires to express his great indebtedness to the Department of Scientific and Industrial Research for grants during the tenures of which this work was carried out; also to Professor F. G. Donnan, F.R.S., at whose suggestion this work was commenced, for his kindly advice and criticism.

THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, March 6th, 1929.*]

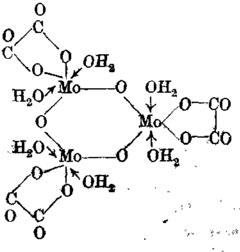
CX.—*Complex Oxalates of Quadrivalent Molybdenum.*

By Henry Mills Spittle and William Wardlaw.

Although molybdenum readily forms a wide range of oxalates, in which the metal has valencies of six, five, four, and three, yet in no case has a normal oxalate been isolated : this is in accordance with the well-known tendency of this element to form oxy-salts. The close relationship existing between the oxalates is shown in the case of the sexa- and quinque-valent derivatives by their co-ordination formulæ, $[MoO_3(C_2O_4),xH_2O](H_2$, HR, or $R_2)$ and $[MoO_2(C_2O_4),yH_2O](H$ or R) (J., 1928, 2742). Knowledge of the oxalates of molybdenum in its lower valency states is still, however, very limited, since there have been isolated but one oxalate, $MoO(C_2O_4),3H_2O$, of quadrivalent molybdenum, and only two of tervalent molybdenum, the soluble $Mo_2O(C_2O_4)_2,6H_2O$ and the insoluble $Mo_4O_3(C_2O_4)_3,12H_2O$ (Wardlaw and Parker, J., 1925, **127**, 1311). By analogy with the co-ordination formulæ used above, it appeared (*loc. cit.*) that the oxalate $MoO(C_2O_4),3H_2O$ could be more adequately formulated as the acid $H_2[MoO_2(C_2O_4),2H_2O]$, *especially* in the light of its pronounced acidic properties.

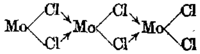
With a view to decide this question, further investigation of the oxalates of quadrivalent molybdenum has been undertaken. In addition to the preparation of molybdenyl oxalate, $MoO(C_2O_4),3H_2O$, and a study of its hydrolytic products, new complex *salts* of the general formula $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$, where R = K, NH_4, or C_5H_6N, have been obtained.

The interesting result emerges from this investigation that, contrary to the original hypothesis, the oxalate $MoO(C_2O_4),3H_2O$ is not satisfactorily formulated as the dibasic acid $H_2[MoO_2(C_2O_4),2H_2O]$ with a co-ordination number of six, but rather as the compound



$H_2[Mo_3O_4(C_2O_4)_3,xH_2O]$

containing a polynuclear complex of three molybdenum atoms. This is supported by the conductivity data, which indicate that the complex oxalates are ternary electrolytes. Amongst the compounds of molybdenum the occurrence of such complexes is not exceptional. The un-ionised acid, $Mo_3O_6(C_2O_4)_3,6H_2O$, corresponding to the salts mentioned above can be conveniently formulated as shown in the annexed figure. In this formula

each atom of molybdenum carries one oxalato-group and two water molecules, and the three molybdenum and three oxygen atoms form a symmetrical 6-membered ring. Such a configuration does not appear improbable in view of the great stability of the new compounds. Ionisation can take place by means of the reaction $Mo \leftarrow OH_2 = [Mo{-}O{-}H]' + H^{\cdot}$. The only point left unexplained is why such a compound can ionise as far as a dibasic acid and no further. It seems comparable with the behaviour of Mo_3Cl_8, in which the peculiar reactivity of two chlorine atoms is still unexplained, although the formula  would account for this property.

The possibility that the metallic atoms may be linked by oxalate radicals rather than by oxygen atoms has been considered, but this leads to a co-ordination number of five for the molybdenum; only by using the oxygen atoms as linkages can a co-ordination number of six be assigned to the metal.

For the oxalates of quinque- and ter-valent molybdenum similar polynuclear complexes, $R_2\left[X(C_2O_4)OMo{<}{}^{O}_{O}{>}MoO(C_2O_4)X\right]$, where $X = C_5H_5N$ or H_2O, and $[3H_2O,(C_2O_4)Mo{-}O{-}Mo(C_2O_4),3H_2O]$, have already been suggested. This tendency of molybdenum to form complex substances containing large numbers of the metal atoms is also seen when molybdenyl oxalate is hydrolysed. Products have been isolated of the empirical formulæ $Mo_5O_6(C_2O_4)_4$ and $Mo_4O_5(C_2O_4)_3$. They appear analogous to the insoluble tervalent oxyoxalate $Mo_4O_3(C_2O_4)_3$, which has been shown to give $Mo_4O_5(C_2O_4)_3$ on *atmospheric oxidation*. Thus a close relationship is now apparent throughout the whole range of the oxalates of molybdenum.

The isolation of an *ammonium salt* of the type

$$R_2[Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_5{\cdot}OH$$

might be adduced as evidence that the complex salts contain a minimum of six molybdenum atoms. In the absence of further convincing evidence in this direction, however, there seems no reason for assigning a more complicated structure to the complex salts.

EXPERIMENTAL.

The simplest method of preparation for the oxalates involves the electrolytic reduction of an acid solution of molybdic acid. This problem is complicated, however, in the case of the oxalates, by the electrolytic reduction of oxalic acid itself, although Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146) states that in oxalic acid solutions of molybdic acid this side reaction has only a very slight influence.

It was found, however, that solutions of tervalent molybdenum thus produced, after oxidation to the quadrivalent state, yielded impure molybdenum oxalates. Accordingly, in the present research, this electrolytic method was discarded in favour of one previously described by Wardlaw and Parker (*loc. cit.*), in which molybdenum trihydroxide, precipitated by addition of ammonia to an electrolytically reduced solution of molybdic acid in sulphuric acid, was dissolved in oxalic acid.

For the preparation of molybdenum trihydroxide the details given in previous communications (*J.*, *1924*, **125**, *1910*; *1925*, **127**, 1311) were followed, but special measures were adopted to remove, as completely as possible, ammonia and ammonium salts. Over a period of 2—3 months, the hydroxide (20 g.) was washed 6 or 7 times with 5 l. of boiling air-free water, by decantation, in an atmosphere of nitrogen. The time required for the settling of the hydroxide was not appreciably affected by the addition of electrolytes, in the form of small quantities of oxalic acid, or a solution of tervalent molybdenum oxyoxalate. The hydroxide, suspended in the smallest possible quantity of water, was then forced on to crystals of oxalic acid (50 g.), just covered with water to displace air, and the mixture heated to give a clear solution. If the brown solution thus produced was boiled in an atmosphere of nitrogen for a considerable period, the brown insoluble tervalent oxyoxalate $Mo_4O_3(C_2O_4)_3,12H_2O$ separated, provided the solution was not concentrated below 150 c.c., and water was added at intervals to make up for that lost by evaporation. On the other hand, by rapid concentration of the solution to 120 c.c., in absence of air, the formation of this insoluble oxalate was avoided, and a deep brown solution resulted, which was cooled, filtered to remove separated oxalic acid, and oxidised at room temperature by the passage of a current of air (free from ammonia). A bright red solution containing quadrivalent molybdenum was obtained (Solution A). It was found undesirable to concentrate this, as boiling caused a colour change to reddish-brown, and the solution so produced did not yield the required product $MoO(C_2O_4),xH_2O$. By addition of the unconcentrated bright red solution to acetone, however, a pinkish-red precipitate of the above composition was obtained, identical in properties with the substance already described (*loc. cit.*).

Salts of the Type $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$.

For the preparation of this series of complex oxalates, alcohol was added to Solution A. No molybdenyl oxalate was precipitated, but a clear blood-red solution resulted, from which the various

complex oxalates described below were obtained by addition of the appropriate base.

Dipyridinium Trimolybdenumtetroxytrioxalate.—To the clear red solution produced by the addition of Solution A (20 c.c.) to alcohol (1000 c.c.), pure pyridine, in sufficient quantity to precipitate 75% of the molybdenum, was added slowly with constant stirring. The bluish-pink flocculent precipitate was collected, washed with alcohol, and dried over calcium chloride in a vacuum {Found : Mo, 33·6; C_2O_4, 30·7; N, 3·26; C, 21·9; H, 2·64. $(C_5H_6N)_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ requires Mo, 33·3; C_2O_4, 30·5; N, 3·24; C, 22·1; H, 2·56%}. In order to determine whether the salt as originally precipitated, and before being dried over calcium chloride in a vacuum, contained associated alcohol, a freshly precipitated sample was air-dried on a porous plate and analysed. Alcohol was thereby shown to be absent. Estimation of valency proved that the molybdenum was quadrivalent.

Analysis. Molybdenum was estimated by direct ignition to the trioxide, or by precipitation as trisulphide and ignition to trioxide (J., 1924, **125**, 1911). Nitrogen was estimated by the method of Dumas, and oxalate as previously described for the oxalates of quinquevalent molybdenum (J., 1928, 2742). In the present research the ignition to trioxide of the $Mo(OH)_4$ obtained during the estimation of oxalate was not found to be satisfactory for the estimation of molybdenum (see p. 796).

Dipotassium Trimolybdenumtetroxytrioxalate.—For the preparation of this salt the method used was similar to that for the pyridinium compound, potassium hydroxide (20%) being added slowly instead of pyridine, in sufficient quantity to precipitate only half the molybdenum present. The product resembled the pyridinium compound in appearance and properties {Found : Mo, 36·7; C_2O_4, 33·4; K, 9·8. $K_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ requires Mo, 36·7; C_2O_4, 33·6; K, 10·0%}.

Diammonium Trimolybdenumtetroxytrioxalate.—Treatment of the clear red liquid produced by the addition of Solution A (10 c.c.) to alcohol (500 c.c.) with ammonia solution (3*N*) in sufficient quantity to precipitate half the molybdenum, resulted in the separation of a bluish-pink precipitate similar to the pyridinium and potassium salts. After being washed with alcohol and dried over calcium chloride in a vacuum, this compound was found by analysis usually to contain a small amount of ammonium oxalate. All the oxalates described above have been precipitated in an amorphous condition. In addition, the ammonium salt has been obtained in the form of purplish-red crystals containing both water and alcohol of crystallisation. For the preparation of this salt, a portion of Solution A

(containing 2 g. Mo) was carefully concentrated on the water-bath to 10 c.c. and dissolved in alcohol (500 c.c.); ammonium oxalate (0·5 g.) was then added in the form of crystals or fine powder. In the latter case the mixture was mechanically agitated for some weeks, and the resulting purplish-red crystals were collected and washed with alcohol. In the former case, after a suitable period, the unchanged crystals of ammonium oxalate were separated from the required red crystals by hand picking. In both cases it was found advisable to re-agitate the product for some days with a freshly prepared alcoholic solution of molybdenyl oxalate, after which the crystals were washed with alcohol and dried in a vacuum over calcium chloride {Found : Mo, 35·5; C_2O_4, 32·7; NH_4, 4·5; C, 13·4; H, 3·5. $(NH_4)_2\ [Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_6O$ requires Mo, 35·5; (C_2O_4), 32·6; NH_4, 4·5; C, 13·3; H, 3·4%}. An exactly similar salt slowly separated from an alcoholic solution of molybdenyl oxalate, to which ammonia or ammonium oxalate solution had been added until there was a faint permanent precipitate. By treatment of alcoholic molybdenyl oxalate solutions with potassium or sodium oxalate or hydroxide solution in a similar manner, very small quantities of crystalline compounds separated, similar in appearance to the ammonium salt described above.

Attempts to make sodium and barium salts, by addition of sodium or barium hydroxide to an alcoholic solution of molybdenyl oxalate, yielded mixtures containing the required salt with the free metallic oxalate.

General Properties.—With the exception of the crystalline ammonium salt, the complex oxalates described above are bluish-pink amorphous solids. They are all very soluble in water, forming bright red solutions, but are insoluble in alcohol or acetone. Addition of alkalis or ammonium oxalate to aqueous solutions of the complex salts gives a blue coloration, but the red colour is restored by the addition of any acid, even acetic. The oxalate ion cannot be detected in aqueous solutions by the usual ionic reactions, nor is molybdenum hydroxide immediately precipitated by the action of alkalis in the cold. Hot potassium hydroxide solution, however, gives a black flocculent precipitate of molybdenum hydroxide, although some of the molybdenum may remain in the solution as the alkali molybdate. If the hydroxide is precipitated by means of sodium hydroxide, it can be obtained in a light green form. Solutions of the complex oxalates possess marked reducing properties, silver nitrate being reduced to metallic silver on boiling. On the addition of lead acetate solution to an aqueous solution of any of the salts, a voluminous bluish-pink precipitate is formed, the colour of which changes on warming to brown.

Molecular-conductivity Determinations.—To decide whether the complex salts $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ are correctly formulated as ternary electrolytes, determinations of molecular conductivity were carried out. Experiments at 0° indicated that the molecular conductivity of aqueous solutions of the complex oxalates did not change with time. This is in accordance with the qualitative observation that in such aqueous solutions neither the oxalate radical nor the molybdenum can be detected by ionic reactions in the cold. The molecular conductivities for dilute solutions at 0° are as follows :

$(NH_4)_2[Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_5{\cdot}OH.$

v	92·7	139·1	208·6	312·9
μ	105·1	124·9	132·0	137·8

$(C_5H_6N)_2[Mo_3O_4(C_2O_4)_3,5H_2O].$

v	71·3	142·6	285·2	570·5	1141
μ	73·6	87·0	101·0	115·9	129·4

It is interesting to note that the lower molecular conductivity of the pyridinium salt is in accordance with the ionic velocities of the pyridinium and ammonium ions, which at 0° are respectively 20 (Lundén, *J. Chim. physique*, 1907, **5**, 592) and 38·4 (Landolt–Börnstein Tabellen, 1923, II, 1104). Moreover, the values for both salts are in agreement with those given by typical ternary electrolytes (J., 1927, 516), although, as would be expected, the large complex anion decreases the values of the molecular conductivity.

Hydrolysis of Molybdenyl Oxalate.

It has already been mentioned that addition of Solution A to acetone yields pinkish-red molybdenyl oxalate with the empirical formula $MoO(C_2O_4),xH_2O$. If, however, Solution A is concentrated by boiling before being added to acetone, a purple product results, of empirical formula $Mo_5O_6(C_2O_4)_4$, and containing both acetone and water. By extraction with aqueous alcohol at room temperature, this compound yields a brown residue of empirical formula $Mo_4O_5(C_2O_4)_3$. These reactions indicate that from molybdenyl oxalate by the action of aqueous acetone or alcohol, various polynuclear molybdenum complexes can be obtained. The probable reactions occurring can be symbolised as follows :

(*a*) $5MoO(C_2O_4) + H_2O \rightleftharpoons Mo_5O_6(C_2O_4)_4 + H_2C_2O_4,$

(*b*) $Mo_5O_6(C_2O_4)_4 \rightleftharpoons Mo_4O_5(C_2O_4)_3 + MoO(C_2O_4),$

or $4Mo_5O_6(C_2O_4)_4 + H_2O \rightleftharpoons 5Mo_4O_5(C_2O_4)_3 + H_2C_2O_4.$

It is interesting to note that the brown product $Mo_4O_5(C_2O_4)_3$ can also be obtained by atmospheric oxidation of a suspension of the insoluble tervalent oxyoxalate, $Mo_4O_3(C_2O_4)_3,12H_2O$, in aqueous or oxalic acid solution.

Pentamolybdenum Hexaoxytetroxalate.—A portion of Solution A (12 g. Mo in 120 c.c.) was concentrated to 40 c.c. by rapid boiling, cooled, filtered from the deposited oxalic acid, and added to acetone (400 c.c.). The dark red oil which separated was treated with dry acetone till granular, collected, and dried over calcium chloride in a vacuum. The *compound* tends to retain acetone, even after long drying, and hence analyses are calculated as molecular ratios [Found: (*a*) Mo, 39·1; C_2O_4, 29·1%; Mo: C_2O_4 = 4·95 : 4·00. (*b*) Mo, 39·0; C_2O_4, 28·8%; Mo : C_2O_4 = 4·98 : 4·00]; it is a purplish-brown crystalline solid, readily soluble in water to a red solution, but insoluble in acetone or alcohol.

Tetramolybdenum Pentoxytrioxalate.—This *compound* can be formed by the addition of the above $Mo_5O_6(C_2O_4)_4$ (1—2 g.) to a mixture of water (8 c.c.) and alcohol (52 c.c.); after shaking and filtration, the resulting brown solid is washed with alcohol and dried over calcium chloride in a vacuum (Found: Mo : C_2O_4 = 4·02 : 3·00, 4·01 : 3·00). A better method for the preparation of this compound is as follows: To a suspension of the insoluble tervalent oxalate (5 g.) in water (30 c.c.), oxalic acid (1 g.) was added. Air (free from ammonia) was drawn through the mixture for 3—4 weeks, and the resulting red solution, without being heated, was filtered and added to acetone (500 c.c.). The light brown precipitate was collected, washed with acetone, and dried in a vacuum over calcium chloride [Found: Mo, 42·1; C_2O_4, 28·8; Mo : C_2O_4 = 4·02 : 3·00. $Mo_4O_5(C_2O_4)_3,10H_2O$ requires Mo, 42·3; C_2O_4, 29·1%]. This compound was proved to contain quadrivalent molybdenum by the usual method of valency determination. As indicated by equations (*a*) and (*b*), it should be possible to convert the above compounds into molybdenyl oxalate, by treatment with appropriate concentrations of oxalic acid. This has been shown to be the case by the following experiment.

Oxalic acid, in slight excess of the theoretical amount, was added to an aqueous solution of either of the above complex molybdenum oxalates. After evaporation to dryness in a vacuum at 50°, the excess oxalic acid was extracted by dry acetone, and the resulting purplish-brown solid dried over calcium chloride in a vacuum [Found: (*a*) Mo, 39·2; C_2O_4, 36·3; Mo : C_2O_4 = 1·00 : 1·01; (*b*) Mo, 39·6; C_2O_4, 36·6; Mo : C_2O_4 = 1·00 : 1·01. Calc. for $MoO(C_2O_4),3H_2O$: Mo, 37·8; C_2O_4, 34·7. Calc. for $MoO(C_2O_4),2H_2O$: Mo, 40·7; C_2O_4, 37·3%]. If too great an excess of oxalic acid is used, the water of crystallisation remaining in the dried mixture of molybdenyl oxalate and oxalic acid forms aqueous acetone, which hydrolyses the product.

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UNIVERSITY OF BIRMINGHAM,
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CXI.—*The Systems* n-*Butyl Alcohol–Water and* n-*Butyl Alcohol–Acetone–Water.*

By DAVID CHARLES JONES.

ORTON and JONES (J., 1919, **115**, 1194) found that a 13·994% hydrochloric acid solution gave with pure n-butyl alcohol an upper and a lower ternary critical solution temperature (*C.S.T.*) of 43·55° and 9·6°, respectively, for the concentrations given in that paper. The complete solubility ring so produced contracts on an increase, and expands on a decrease, in the concentration of the hydrochloric acid solution. The ternary *C.S.T.*'s with hydrochloric acid solution were extremely sensitive to typical impurities in the n-butyl alcohol, and the data were utilised in following the purification of n-butyl alcohol, obtained from various sources; the method thus devised proved to be far more sensitive to most impurities (except water) than those based on any other physical property, and in order to obtain a specimen of the alcohol which was so pure that all its fractions behaved uniformly according to this criterion, it was necessary to prepare a crystalline derivative and subsequently regenerate the alcohol.

The solubilities of isomeric alcohols, such as the butyl alcohols, are of considerable theoretical interest, and it was therefore decided to determine the binary solubility curve with water of n-butyl alcohol thus purified, the purity having been confirmed by the use of this sensitive criterion. The ternary system n-butyl alcohol–acetone–water was also investigated from −15° to the temperature of the binary *C.S.T.*, *viz.*, 124·74°, and in all cases the ternary *C.S.T.*'s were far more sensitive to impurities than the binary.

The System n-*Butyl Alcohol–Water.*

The n-butyl alcohol was prepared as before (Orton and Jones, *loc. cit.*), and dried with calcium oxide before the final fractional distillation through a twelve-bulb pear still-head. The several fractions gave identical *C.S.T.*'s with a hydrochloric acid solution. The values for the density and refractive index of the pure material

were $D_{14\cdot4^\circ}^{14\cdot4^\circ}$ 0·81417 and $n_C^{20\cdot0^\circ}$ 1·39711. The water was freshly boiled conductivity water obtained from a Bousfield still. The synthetic method of determining the solubility points was used, and the experimental details were essentially as described by Jones and Betts (J., 1928, 1179). It was found that ordinary soda glass, even if well steamed, could not be used for accurate determinations, for redeterminations just above 120° gave readings as much as 1° higher. This did not occur with well-steamed Pyrex glass, even if readings were repeated during a period of several months, and tubes of this glass were used, since the readings obtained were identical with those in control experiments with quartz-glass tubes in the neighbourhood of the *C.S.T.* The thermometer was tested, during the period when the work was done, at the National Physical Laboratory. The results are given in Table I (where *u* and *l* refer to upper and lower miscibility temperatures obtained with the same concentration of solution) and shown graphically in Fig. 1, Curve 1.

TABLE I.

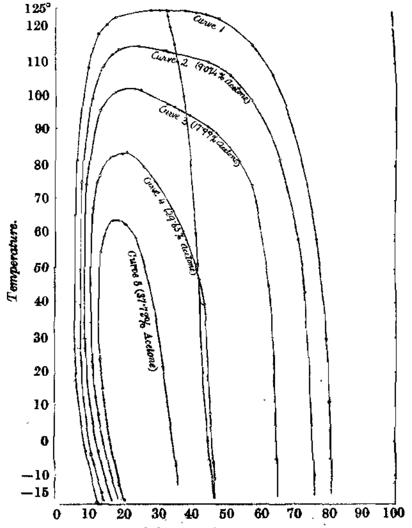
$n\text{-}C_4H_{10}O$, %	6·03 [1]	6·47 [2]	9·79 [3]	12·72 [4]	15·15 [5]	17·51 [4]
Temp.	65·0° *u*	81·0° *u*	107·72° *u*	117·40° *u*	120·30°	122·45°
	40·0° *l*	19·3° *l*	−3·11° *l*	−18·01° *l*		
$n\text{-}C_4H_{10}O$, %	27·38	28·16 [6]	30·39 [7]	32·49 [8]	32·85 [9]	33·79 [5]
Temp.	124·74°	124·74°	124·73°	124·74°	124·75°	124·72°
$n\text{-}C_4H_{10}O$, %	38·05 [6]	41·30 [10]	44·03	48·01	57·80	63·44
Temp.	124·66°	124·05°	123·75°	122·60°	115·00°	106·05°
$n\text{-}C_4H_{10}O$, %	76·27	79·51 [11]	80·46	80·82 [11]		
Temp.	58·50°	29·82°	13·0°	−5·0°		

[1] *Accuracy* ±2°; *slightly cloudy between these temperatures.*
[2] Accuracy ±2°.
[3] Rising temperature, 107·72°; falling, 107·60°.
[4] Observation accurate to 0·02°; rising and falling temperatures identical within these limits of accuracy. This applies to all the following determinations until the system containing 79·51% of *n*-butyl alcohol is reached.
[5] Repeated after three months.
[6] *Slight critical* opalescence; striations almost absent.
[7] Lower layer very large.
[8] Equal volumes; clearest critical phenomena.
[9] Upper layer greater than lower; quartz experimental tube.
[10] Determinations made at intervals up to eight days; no change observed even after heating to a temperature of 130°.
[11] Accuracy of determination 0·1°; difference of 1° between rising and falling temperatures.

The upper portion of the curve is flat, no change of miscibility temperature exceeding 0·02° being detectable within the concentration limits 28—34% of *n*-butyl alcohol. From the extrapolation of the mean concentration line, the critical solution concentration is 32·4% *n*-butyl alcohol. Several points were determined in the

immediate neighbourhood of the *C.S.T.* in cylindrical Pyrex-glass tubes, and an endeavour was made to determine the critical concentration by the direct readings of the volumes of the phases. The 32·49% mixture gave layers of almost equal volume, the 32·85% mixture a greater upper layer, and the 30·39% a much

FIG. 1.



% n-*Butyl alcohol* (*curve* 1).
% n-*Butyl alcohol* + *acetone mixture* (*curves* 2—5).

greater lower layer. The 32·4% *n*-butyl alcohol corresponds to a molar fraction of 0·1044, or 10·44 mols.%.

The *C.S.T.* is at 124·75°, which is lower than that given by Hill and Malisoff (*J. Amer. Chem. Soc.*, 1926, **48**, 924), *viz.*, 125·15°. Such a difference would be easily possible if these authors used ordinary glass. Alternatively, although their specimen boiled constantly within 0·1°, it may have contained a trace of impurity, for certain impurities, if they happen to be present in the original

sample, can scarcely be removed by even prolonged distillation methods (Orton and Jones, *loc. cit.*); on the other hand, this binary *C.S.T.* is very insensitive to typical impurities. Other sensible deviations from the determinations of Hill and Malisoff occur mainly in the portion of the curve representing the water-rich phase; thus, at 20° the value obtained was 6·5% of *n*-butyl alcohol, whereas Hill and Malisoff give 7·81%, a value apparently corroborated by the determination of Reilly and Ralph, *viz.*, 7·90% (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 597). The last two values, however, were both obtained by a volume method, and it is possible that at least a part of the discrepancy may be due to the difficulty of separating the phases accurately—frequently thin emulsions persist for a very long time. That Reilly and Ralph's value is really confirmatory, however, is to be doubted, since they state that the saturated solution of the alcohol in water, as prepared, was sligbtly cloudy, but on raising the temperature this cloudiness disappeared—owing to the minimum on the solubility curve, the solution should have become *more* cloudy under these conditions.

The solubility curve was followed as far below the freezing-point curve as possible, in order to determine whether a metastable lower *C.S.T.* could be observed, or whether the system was similar to that of methyl ethyl ketone–water (with maxima of mutual insolubility on both arms) or to that of *sec.*-hutyl alcohol–water, where some workers have found a waist in the curve (Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129; Dolgolenko, *ibid.*, 1908, **62**, 499). It was possible to follow the solubility curve to approximately − 20°, *i.e.*, 17° below the invariant freezing point of the two-layer system. As is evident from the curve, the solubility in water of the *n*-butyl alcohol increases very rapidly as the temperature falls, but no maximum of mutual insolubility, such as occurs at approximately 52° with the water-rich phase, occurs on the other arm of the curve, even down to − 20°.

The mean-concentration curve, which from 50° up to the *C.S.T.* is slightly curved, bending as is usual towards the axis representing the more volatile component, shows at about 50° a point of inflexion, and from this point to lower temperatures it moves at an increasing rate towards a greater concentration of *n*-butyl alcohol. It will be seen that at −15° the mean concentration has already reached a value of 46·5% of alcohol. This is the behaviour that would be expected if the lower terminus of the line were at a hypothetical lower *C.S.T.*

Table II contains the solubility results (read from an enlargement of Fig. 1) from which the points on the mean-concentration line were calculated; S_w and S_a represent respectively the percen-

tages of the alcohol in the water-rich and alcohol-rich phases, and the fourth column gives the mean.

TABLE II.

Temp.	S_w.	S_a.	Mean.	Temp.	S_w.	S_a.	Mean.
124·75°	32·4	32·4	32·4	80°	6·4	72·7	39·6
123	19·0	46·8	32·9	60	6·0	76·2	41·1
120	14·7	52·5	33·6	40	6·0	78·6	42·3
115	11·7	57·8	34·75	20	6·4	80·2	43·3
110	10·2	61·5	35·85	0	9·1	80·6	44·85
100	8·2	66·4	37·3	−15	12·0	81·0	46·5

Discussion.—The butyl alcohols are in the following order with regard to their *C.S.T.*'s with water : *iso*>*n*>*sec.*>*tert.* The same order obtains for the *iso-* and *n*-butyric acids, but it is reversed in the corresponding aldehydes. Below 60°, *iso*butyl alcohol is more soluble than the *n*-alcohol in water, the curves crossing at about this temperature.

The extent of the mutual solubility of two liquids is determined by two factors : (1) the relative intermolecular attractions between the molecules of the same kind, and that between the molecules of different kinds, and (2) any chemical combination between the molecules of different kinds.

It is very probable that the mutual solubility of alcohols and water is due to both these factors ; (1) is endothermic, and becomes predominant as the temperature is raised, whilst (2) is exothermic, and predominates at lower temperatures. As a result, there is a maximum of mutual insolubility, such as is observed at 52° in the case of *n*-butyl alcohol and water. The mutual solubility of alcohols in saturated hydrocarbons must be ascribed to (1) alone; in no case of this kind does the solubility increase with fall of temperature.

It is possible that the mutual solubilities of the ethers and water provide an illustration of effect (2) alone. Thus, it is a remarkable fact that, if the first few members of both series be neglected, the ethers have very similar boiling points to the saturated hydrocarbons of approximately the same molecular weight, *e.g.*,

	M.	B. p.		*M.*	B. p.
$CH_3·O·C_4H_9$ ...	88	70·3°	C_6H_{14}	86	68·9°
$CH_3·O·C_7H_{15}$ ...	130	149·8	C_9H_{20}	128	149·5
$CH_3·O·C_8H_{17}$ ...	144	173·0	$C_{10}H_{22}$	142	173·0

(Kauffmann, "Beziehungen zwischen physikalischen Eigenschaften und Chemischer Konstitution," 1920, p. 151.)

The same similarity occurs between the boiling points of the isomeric hexanes and the corresponding methyl butyl ethers (Bennett and Philip, J., 1928, 1930) :

n-Hexane	68·9°	Methyl *n*-butyl ether	70·0°
β-Methylpentane	62·0	Methyl *iso*butyl ether	58·0
γ-Methylpentane	64·0	Methyl *sec.*-butyl ether	59·0
ββ-Dimethylbutane	49·6	Methyl *tert.*-butyl ether	54·0

Thus the introduction of ethereal oxygen into a hydrocarbon apparently does not increase the mutual attraction of the molecules. It is possible, therefore, that apart from factor (2) the ethers would be as insoluble in water as the hydrocarbons. In that case the mutual solubility of the ethers is dependent on the formation of hydrates, their distribution between the ethereal and aqueous phases, and their consequent mutual solvent effects. The ether hydrates should be distributed far more in the aqueous phase, and this would account for the much larger solubilities of the ethers in water than of water in the ethers. Moreover, this hypothesis explains the form of the solubility curves. The reversible heat of solution is positive in all cases in the aqueous phase, and it is quite possible that the variable slope, sometimes positive, sometimes negative, of the ether-rich phase is due to the superposition of the two effects, (i) positive heat of solution due to hydrate formation, and (ii) the negative heat of solution due to mutual solvent action. Bennett and Philip (*loc. cit.*) have made some interesting speculations regarding the solubilities of methyl butyl ethers in water, explaining the extent of this as due to the Harkins–Langmuir effect of the length of the hydrocarbon chain, and to the electron-repelling effects of the positive alkyl groups attached to the oxygen.

Harkins (see, *e.g.*, Harkins and King, *J. Amer. Chem. Soc.*, 1919, **41**, 970) has shown, from surface-energy considerations, that the attraction of hydrocarbon for hydrocarbon is less than that of hydrocarbon for hydroxyl. By similar reasoning, the solubility of *n*-butyl alcohol in water, neglecting hydration, would be mainly determined by (*a*) the very large attraction of the hydroxyl groups of water for those of the alcohols, (*b*) the smaller, but still considerable attraction of the alkyl groups of the alcohol for water, and (*c*) the very large attraction of the water molecules for one another. The length of the hydrocarbon chain attached to the hydroxyl of the alcohol has a large effect on the solubility, owing, mainly, to (*c*), because any solution of alcohol in water means the substitution of a hydrocarbon–water interface for a water–water interface.

As regards factor (2), *i.e.*, the extent of hydrate formation, any definite conclusion is a matter of great difficulty. Bennett and Philip (*loc. cit.*) have put forward the view that, in the case of the methyl butyl ethers, increased electron-repelling effects of the secondary and tertiary radicals (see Allan, Oxford, Robinson, and Smith, J., 1926, 401) increase the tendency of the oxygen of the ethers to donate a lone pair of electrons to the hydrogen of the

water, and thus increase the hydration and the solubilities of these ethers in water (see Sidgwick, "The Electronic Theory of Valency," p. 137).

Applying these views to the isomeric butyl alcohols, we can say that, neglecting factor (2), there is sufficient decrease in the hydrocarbon–water interface between *n*- or *iso*-butyl alcohol and *tert*.-butyl alcohol to account for the difference in the solubility in water, *e.g.*, the hydrocarbon–water interface in *tert*.-butyl alcohol is not much greater than that of *n*-propyl alcohol, which is completely miscible with water.

It is very probable that the solubility curves of *iso*- and *sec*.-butyl alcohol have not been obtained with the pure substances (see Timmermans, *loc. cit.*, and Dolgolenko, *loc. cit.*). However, the experimental values available indicate that *iso*butyl alcohol is slightly more soluble in water than *n*-butyl alcohol at ordinary temperatures, but it has a higher *C.S.T.* (*viz.*, 133°), and this can be ascribed quite clearly to the very large difference in solubility of *water* in the alcohols (at 20° its solubility in *n*-butyl alcohol is 20%, and in *iso*butyl alcohol 16%).

The *C.S.T.* of *sec*.-butyl alcohol is 115°, *i.e.*, 9·7° below that of *n*-butyl alcohol, but there are very marked maxima of mutual insolubility on both arms of its curve, so that at ordinary temperatures the *sec*.- has a very much larger solubility than the *n*-compound (at 20° the solubility of the *sec*.-alcohol is 37%). If the results at the lower temperatures are not due to an impurity acting as a mutual solvent, there would appear to be distinct evidence here of a large hydrate formation, which may be evidence of the electron-repelling effect of a secondary alkyl group of a similar character to that to which the high dissociation constant of the secondary amines has been ascribed. The solubility results at the higher temperatures are qualitatively what would be expected from the decreased hydrocarbon–water interface.

It is of interest to examine the available physicochemical evidence for the electron-repelling effect of alkyl groupings similar to those present in the butyl alcohols. The dissociation constants of the isomeric aliphatic acids should afford information; thus, the four C_5 acids have the same alkyl groups as are present in the butyl alcohols, and the dissociation constants (Kauffmann, *loc. cit.*) are *n*-valeric acid 0·00161; methylethylacetic acid 0·00168; *iso*valeric acid 0·00173; trimethylacetic acid 0·000978.

The tertiary radical is acting in an electron-repelling character, but this is not evident in the case of the *iso*- or *sec*.-butyl radical. Butyric and *iso*butyric acids have almost the same values, and in the C_8 acids the same marked fall in the constant occurs when a

tertiary alkyl radical is present, *i.e.*, in dimethylethylacetic acid: but in diethylacetic acid, where a secondary radical is present, the dissociation constant (0·00203) is greater than that of *n*-hexoic acid (0·00146). In the case of the amines, on the other hand, the secondary amine is stronger than either the primary or the tertiary (*Moore and Winmill, J.*, *1907*, **91**, *1373*; *1912*, **101**, *1635*).

The evidence in other directions is unfortunately ambiguous; for example, since the mechanisms of association and of hydration are similar, both effects involving donation from oxygen to the hydrogen of another alcohol molecule in the one case and to the hydrogen of water in the other, it might be thought that there would be a connexion between the two, in the sense that the more associated alcohol would be hydrated to a greater extent. Biltz (*Z. physikal. Chem.*, *1899*, **29**, *249*) determined cryoscopically the relative association of these alcohols in dilute benzene solution, and concluded that the relative association is in the order *n*>*sec.*>*tert.* This could not be due to the greater positivity of the vapour-pressure curves of, *e.g.*, the tertiary alcohol, because this alcohol would be much less soluble in non-polar solvents such as benzene.

The boiling points of these isomeric alcohols lead to the same conclusion about the extent of association as the cryoscopic results recorded above. Branching of the carbon chains in the hydrocarbon produces a lowering of the boiling point, but the difference in the boiling points of the butyl alcohols is much greater than would be expected from the branching of the chain alone. [The boiling points are *n*-, 117°; *iso*-, 107·5°; *sec.*-, 99°; *tert.*-, 82·9°. Compare with these the values given for the corresponding hexanes and methyl butyl ethers (p. 804).] The high boiling points of alcohols as compared with hydrocarbons or ethers are probably due to a physical attraction between the hydroxyl groups, and to the association as well. It is difficult to ascribe the high value of the critical pressure and of the van der Waals constant *a* to association alone (Berthoud, *J. Chim. physique*, 1918, **16**, 245). Branching of the hydrocarbon chain in the alcohols tends, therefore, not only to reduce the mutual attraction of the hydrocarbon portions of the molecule for one another, as in the hexanes, but also to produce a greater normalising tendency. However, one cannot be sure that this latter effect is due to a decrease in the donative powers of the oxygen, for the increased negativity of the oxygen might affect adversely the acceptor properties of the hydrogen in another alcohol molecule. This effect would not occur in hydration. Moreover, steric effects may be important in the association.

The dielectric constants of these alcohols are in the order *n*(ϵ = 19·2)>*iso*>*sec.*>*tert.* (ϵ = 11·4). Thus they afford an illustration

of a very unusual effect, since, especially with isomerides, the higher solubilities in water usually accompany the larger values of ε. Smyth (*J. Amer. Chem. Soc.*, 1924, **46**, 215) has calculated the dipole moments of these alcohols, and they are in the order *n*, *iso*$>$*sec.*$>$*tert.*, but the differences between the values are small. An increased electron-repelling effect due to the secondary or tertiary alkyl groups would tend of itself to *increase* the electric moment, the centre of gravity of the negative charge being displaced nearer to the nucleus of the oxygen atom; but this effect may be outbalanced by an increase in the angle of attachment of the two positive groups, hydrogen and alkyl, with a consequent decrease in the distance between the centres of gravity of the positive and negative charges. It would appear, therefore, that at present any attempt to place the butyl alcohols in their relative order of extent of hydration would be of little value.

Two interesting results which follow from the study of the mutual solubilities of two liquids, of which one is water, may be mentioned here. (1) If the concentration of the components in the coexisting phases are expressed as g.-mols.%, the water has in all cases a much greater solubility in the phase rich in the second component than has the second component in the water-rich phase. (2) If one compares the solubility of water in oxygen-containing compounds which have about the same solubility in the water-rich phase, it is evident that they are clearly divisible into two groups: water is much more soluble in those compounds that contain a hydroxyl group, *e.g.*, alcohols, phenols, and carboxylic acids. Table III

TABLE III.

Second component.	Temp.	S_a.	S_b.	A_2.	B_1.	A_2/B_1.	ϕ_A/ϕ_B.
Methyl ethyl ketone	20°	24·00	10·00	0·074	0·306	0·241	0·48
sec.-Butyl alcohol ...	20	20·00	37·00	0·057	0·708	0·081	
*iso*Butyric acid	20	22·8	44·6	0·057	0·798	0·071	1·04
Acetylacetone	30	15·5	5·0	0·031	0·225	0·142	0·70
Ethyl acetate	20	8·53	3·07	0·016	0·152	0·106	0·68
Ethyl ether	20	6·95	1·20	0·022	0·048	0·469	0·41
n-Butyl alcohol	20	6·50	20·00	0·015	0·507	0·030	
Phenol	20	8·3	28·0	0·017	0·670	0·025	
Furfuraldehyde	40	8·2	6·3	0·016	0·265	0·062	
Benzoic acid	70	6·0	17·0	0·009	0·582	0·016	1·21
Salicylic acid	70	8·0	36·0	0·011	0·809	0·014	

summarises some of the results; S_a is the solubility of the second component in water, and S_b that of water in the second component, both as g. per 100 g. of solution; A_2 and B_1 are the corresponding mol. fractions.

The first four materials mentioned in the table have a large solubility in water, but the values given show how much more soluble water is in the compound-rich phase when the compound

contains a hydroxyl group. The results for acetylacetone are interesting; the low solubility of water in this compound is clear additional evidence for the absence of the hydroxyl groups owing to the chelate ring structure. The other materials in the table are typical oxygen-containing compounds, having a solubility in water of 6—8%. It is obvious that, in the case of the alcohols, phenols, and acids, water has a very great solubility in the compound-rich phase. The values for salicylic acid and ether ($A_2/B_1 = 0{\cdot}014$ and $0{\cdot}469$, respectively) are especially striking. In all cases, as the fractional value of A_2/B_1 shows, the mol. fraction of the water in the compound-rich phase is greater than that of the compound in the water-rich phase.

In any comparison of the solubilities of a series of liquids with another liquid, such as water, the extent of the solubility will depend considerably on the composition of the phase which is in equilibrium with the water-rich phase. The solubility of one pure liquid in another cannot be determined directly, as can the solubility of a solid in a liquid. Langmuir (*Colloid Symposium Monograph*, 1925, 3, 62) has applied his theory of " independent surface action " to the case of mutual liquid solubility, and, making use of Boltzmann's equation, has derived the formulæ

$$(1)\ \frac{A_1}{A_2} = e^{\frac{S_A\phi_A}{kT}(\beta_2^2 - \beta_1^2)}; \qquad (2)\ \frac{B_1}{B_2} = e^{\frac{S_B\phi_B}{kT}(\alpha_2^2 - \alpha_1^2)}.$$

The subscripts 1 and 2 refer to the two liquid phases concerned. A and B are *the mol. fractions*, and α and β *the surface fractions* of the two liquid components; S_A and S_B are their molecular surfaces; k is Boltzmann's constant, and T the absolute temperature. The symbol ϕ *is a function of the partial interfacial surface tensions* exerted between the various groups in the molecules of the liquids, and should give the same value in both equations, *i.e.*, if calculated *from the distribution of either component in phases* 1 and 2. The distribution of A between the two phases will be markedly affected by the relative distribution of B; this is covered by the term $(\beta_2^2 - \beta_1^2)$. The low values of A_2/B_1 are accounted for by the relatively small surface area of the water molecule. In Table III the ratio ϕ_A/ϕ_B is given for a few typical cases. This ratio should be equal to unity, and any deviation may be ascribed to effects such as hydration and association, which are not taken into account in the derivation of the formulæ. It will be noticed that substances which give a high value for A_2/B_1 give a very low value for this ratio, *e.g.*, methyl ethyl ketone and ethyl ether, whereas benzoic acid and *n*-butyl alcohol, and to a less extent isobutyric acid, give a value greater than unity. Values less than unity would mean that water

has a smaller solubility in the second component-rich phase than it theoretically should, and values greater than unity denote a too great concentration of water in this phase. Possibly these deviations may be due to hydrate formation, and subsequent distribution between the two layers. In the case of ethyl ether this hydrate may be distributed largely in the aqueous phase, whereas in the compound containing a hydroxyl group there would be a much more even distribution between the two phases. The calculations show that even in the case of n-butyl alcohol the very great disparity in the solubility of the two components in one another (S_a and S_b) is largely accounted for on this theory by the difference in the molecular surface extents.

The System n-*Butyl Alcohol–Acetone–Water.*

Since the binary solubility curve has only one maximum of mutual insolubility, it was of interest to determine the effect of a third component that would act as a mutual solvent. For this purpose acetone was chosen, and the ternary system was studied in sufficient detail to construct the complete binodal surface, from the binary *C.S.T.* at 124·74° down to −15°.

The acetone used for these determinations was A.R. material (B.D.H.). It was purified as described by Reilly and Ralph (*loc. cit.*), and redistilled several times through a six-foot fractionating column of the type described by Clarke and Rahrs (*J. Ind. Eng. Chem.*, 1923, **15**, 349). It had b. p. 56·3°/760 mm. The method adopted was as follows: Mixtures of n-butyl alcohol with various proportions of acetone were made up by weight, and the solubility curve of each of these mixtures with water was determined by the synthetic method; the curves thus obtained are shown in Fig. 1 (curves 2 to 5), the abscissæ representing the percentage by weight of the acetone–n-butyl alcohol mixture. The actual values obtained are given in Table IV. From these curves the binodal curves for the system can be constructed as on the triangular diagram in Fig. 2. This is done in the following way: Table V shows the miscibility concentrations read from the curves 2 to 5 in Fig. 1, at the various temperatures indicated. Thus when the mixture contained 9·07% of acetone, from curve 2 are read the miscibility concentrations at 25°, *i.e.*, 7·9% and 75% of the mixture. The water present is therefore 92·1% and 25% respectively. In the ternary diagram (Fig. 2), all systems composed of the 9·07% mixture and varying proportions of water will lie on the line joining the water apex to the point X representing the composition 9·07% acetone, 90·93% n-butyl alcohol. At 25° the two miscibility points will lie on the intersection of this line and the lines LM and NO parallel to the

base and representing 92·1% and 25% of water respectively; α and β therefore represent two points on the binodal curve for 25°. *Each mixture will give two such other points and thus the isotherm* can be plotted. Fig. 2 shows the isotherms for five chosen temperatures. KK′ is the critical curve. This method provides a very simple and accurate method for plotting the binodal curves at any desired temperature. The binodal curve at 20° is in good agreement with the determination of Reilly and Ralph (*loc. cit.*)

FIG. 2.

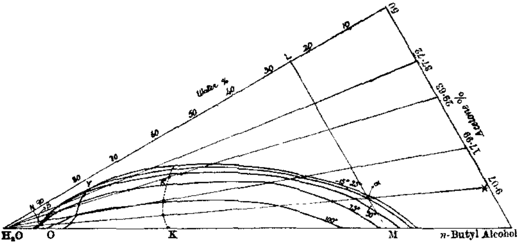


TABLE IV.

9·07% Acetone in n-butyl alcohol.		17·99% Acetone in n-butyl alcohol.		29·63% Acetone in n-butyl alcohol.		37·72% Acetone in n-butyl alcohol.	
% Mixture.	Temp.	% Mixture.	Temp.	% Mixture.	Temp.	% Mixture.	Temp.
7·82	74·8° *u*	9·15	73·8° *u*	11·13	67·10° *u*	13·54	54·5° *u*
	app. 30·0 *l*		26·1 *l*		23·01 *l*		23·5 *l*
10·73	98·7 *u*	13·16	95·5 *u*	12·32	74·85 *u*	14·34	58·7 *u*
	−4·0 *l*		−3·2 *l*		12·5 *l*		15·0 *l*
13·56	107·5 *u*	17·25	100·8 *u*	13·19	76·6 *u*	18·83	63·7 *u*
	−14·0 *l*		−12·0 *l*		7·4 *l*		−13·0 *l*
14·09	108·3 *u*	24·80	101·6	16·17	81·8 *u*	20·52	62·5 *u*
	−15·0 *l*				−8·6 *l*		−17·0 *l*
16·71	111·6 *u*	32·57	97·65 [3]	19·68	82·9 *u*	23·55	58·5
	below −20·0 *l*				below −19 *l*		
18·57	113·1	34·69	96·75 [1,2]	21·01	83·85	31·71	21·2
24·46	114·15	39·22	94·3 [1]	25·84	79·35	35·52	−7·0 [3]
31·59	112·9 [1,3]	44·43	91·1	28·99	75·1		
32·47	112·9 [1,2]	54·02	80·85	37·52	60·75		
44·98	109·7	57·55	74·2	38·31	58·15 [1,2]		
51·19	106·1	62·30	45·1	42·16	46·45		
57·25	98·9	65·0	−5·2	43·54	39·40		
65·66	81·7			45·47	7·65		
71·20	58·4			46·60	−11·00		
73·15	43·0						
75·70	−10·0						

[1] Critical phenomena very distinct. [2] Very close to equal volumes.
[3] Lower layer greater.

with the exception of the portion representing the high concentrations of water. The actual composition of the ternary mixtures at each point represented on Fig. 2 is given in Table V.

TABLE V.

% Acetone in mixture used.		$T = -15°$.		$T = 25°$.		$T = 50°$.		$T = 75°$.		$T = 100°$	
		%	%	%	%	%	%	%	%	%	%
0	Water	19·1	87·9	20·16	93·8	22·53	94·0	26·30	93·78	33·60	91·33
	Acetone	0	0	0	0	0	0	0	0	0	0
	n-$C_4H_{10}O$	80·9	12·1	79·84	6·2	77·47	6·0	73·70	6·22	66·4	8·67
9·07	Water	24·0	86·0	25·0	92·1	27·6	92·4	32·4	92·18	43·5	89·05
	Acetone	6·89	1·27	6·8	0·72	6·57	0·69	6·13	0·71	5·12	0·99
	n-$C_4H_{10}O$	69·10	12·73	68·2	7·18	65·83	6·91	61·47	7·10	51·38	9·96
17·99	Water	34·9	83·9	36·2	90·85	38·45	91·4	42·75	90·8	71·57	84·64
	Acetone	11·71	2·90	11·48	1·65	11·08	1·55	10·30	1·66	5·12	2·76
	n-$C_4H_{10}O$	53·39	13·20	52·32	7·50	50·47	7·05	46·95	7·54	23·31	12·60
29·63	Water	54·0	82·2	55·45	88·87	58·8	89·24	71·01	86·81		
	Acetone	13·63	5·27	13·20	3·30	12·21	3·19	8·59	3·91		
	n-$C_4H_{10}O$	32·37	12·53	31·35	7·63	28·99	7·57	20·40	9·28		
37·72	Water	64·1	80·5	69·00	86·52	74·02	86·68				
	Acetone	13·54	7·35	11·69	5·08	9·80	5·02				
	n-$C_4H_{10}O$	22·36	12·15	19·31	8·40	16·18	8·30				

From the projections of the various binodal curves in Fig. 2, the effect of acetone at the various temperatures can be visualised. The isotherms cross one another only in the small region at the left-hand side of the diagram, representing the systems containing a high percentage of water. Only systems having a composition within this region would show a lower miscibility point above $-15°$, and points in this area are far removed from the critical region. The $-15°$ and $25°$ isotherms cut at the point Y, representing a system having the composition 78% water, 9% acetone, and 13% n-butyl alcohol.

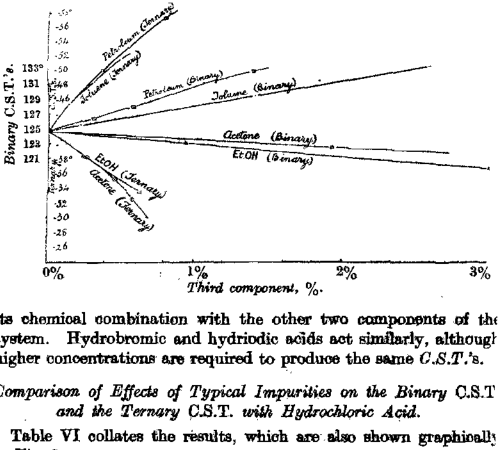
The acetone behaves as would be expected of a third component that acts purely as a mutual solvent for the other two. It becomes increasingly more effective as its concentration in the system increases, so that the critical line falls quite slowly from the binary *C.S.T.*, and then curves and falls increasingly steeply down to $-15°$. Except in the small region mentioned above, a fall of temperature is always accompanied by a decrease of solubility. This is shown also by the various vertical sections of the binodal surface that are represented by the curves 2 to 5 in Fig. 1, *i.e.*, no addition of acetone produces a maximum on that portion of the solubility curve representing saturated solutions rich in n-butyl alcohol. Thus, as shown on Fig. 1, curve 5, even when the upper *C.S.T.* has fallen below $-15°$ there is no maximum on the right-hand arm of the curve. No solubility ring is produced which possesses critical points.

It must be concluded either that the binary solubility curve has no lower metastable *C.S.T.* and the complete solubility ring cannot

be assumed present in the system, or that such a lower *C.S.T.* is at an extremely low temperature.

Other mutual solvents, such as ethyl alcohol and acetic acid, were examined qualitatively, and gave the same results as did acetone. No complete solubility ring was formed, and only one maximum of mutual insolubility was present on the arm of the curve representing the phase rich in water, even with the highest concentrations of the third component. It has been shown, however (Orton and Jones, *loc. cit.*), that hydrochloric acid as a third component would produce a complete ring containing an upper and a lower *C.S.T.* It seems very probable that this is an effect due, not to the mutual solvent action of the third component, but rather to

Fig. 3.



its chemical combination with the other two components of the system. Hydrobromic and hydriodic acids act similarly, although higher concentrations are required to produce the same *C.S.T.*'s.

Comparison of Effects of Typical Impurities on the Binary C.S.T *and the Ternary* C.S.T. *with Hydrochloric Acid.*

Table VI collates the results, which are also shown graphically in *Fig.* 3.

It will be seen that the ternary *C.S.T.* is extremely sensitive to typical impurities in the alcohol, *e.g.*, 1% of acetone produces a decrease of approximately 20° in the upper ternary *C.S.T.*, and of only 1·14° in the binary *C.S.T.*; the results for 1% petroleum show an increase of approximately 19° and 5°, respectively. The figures given show plainly that a binary *C.S.T.* cannot be regarded as a trustworthy criterion of the purity of a liquid. Only for certain

TABLE VI.

Comparison of the effect of impurities on the ternary and binary C.S.T.'s.

	Ternary *C.S.T.*				Binary *C.S.T.*					
% Acetone	0	0·202	0·437	0·575	0	1·92	0·07	18·02	29·53	37·73
C.S.T. *u*	41·90°	38·40°	35·35°	32·66°	124·75°	122·72°	112·90°	96·75°	58·13°	$<-15°$
l	11·84	15·25	18·25	21·00						
% Petroleum	0	0·377	0·799		0	0·310	0·581	1·405		
C.S.T. *u*	41·90°	49·06°	57·10°		124·75°	126·55°	128·10°	132·92°		
l	11·84	4·45	0·35							
% EtOH	0	0·238	0·629		0	0·927	3·78	23·8	35·22	47·65
C.S.T. *u*	41·90°	38·45°	33·65°		124·75°	123·30°	118·40°	74·70°	38·46°	3·70°
l	11·84	15·10	19·10							
% Toluene	0	0·142	0·316	0·508	0	1·406	2·586			
C.S.T. *u*	41·90°	45·75°	48·45°	51·55°	124·75°	129·63°	133·55°			
l	11·84	8·10	5·45	—						

The petroleum had b. p. 171—175°; purification of this specimen is described by Jones and Betts (*loc. cit.*, p. 1179).
u = Upper *C.S.T.* *l* = Lower *C.S.T.*

impurities in certain particular liquid pairs do we find this property valuable in this connexion, and then it is frequently of great sensitiveness. Ternary *C.S.T.*'s are of much more general use for this purpose.

The results show that the specimen of *n*-butyl alcohol used in this work was of a high degree of purity. In fact the criterion of purity used was much more sensitive than was necessary for the determination of the binary *C.S.T.* constants of the *n*-butyl alcohol.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, January 30th*, 1929.]

NOTES.

9-*Benzhydrylanthrone and iso Dianthranyl.* By EDWARD DE BARRY BARNETT and NORMAN FREDERICK GOODWAY.

9-*Benzhydrylanthrone.*—Anthrone (8 g.), potassium hydroxide (100 c.c. of 25% solution), and crude benzhydryl chloride (20 c.c.) were boiled (about 20 minutes) until the colour of the solution became pale: it was found to be inadvisable to carry the heating beyond this point. The product was cooled, washed with water, triturated with ether, and recrystallised from glacial acetic acid and from benzene–light petroleum; it was then colourless and melted at 188—189° (Found: C, 89·9; H, 5·7. $C_{27}H_{20}O$ requires C, 90·0; H, 5·5%). This *benzhydrylanthrone*, when heated on the water-bath with pyridine and acetic anhydride, yielded 9-benzhydryl-anthranyl acetate which, after recrystallisation from glacial acetic acid, melted at 234—235°, and not at 228—229° as stated by

Padova (*Compt. rend.*, 1909, **149**, 219; *Ann. Chim.*, 1910, **19**, 393), who obtained it by boiling diphenylmethyleneanthrone with zinc dust, sodium acetate, and acetic anhydride.

iso*Dianthranyl.*—Benzhydrylanthrone (10 g.) and zinc dust (20 g.) were boiled with 100 c.c. of glacial acetic acid and 20 c.c. of concentrated hydrochloric acid, added during 45 minutes. After boiling for a further period of one hour, the hot solution was filtered and the crystals which separated on cooling were recrystallised twice from glacial acetic acid containing a little hydrochloric acid and twice from toluene. The pale yellow, crystalline product melted at 312° after some decomposition at about 308° (Found: C, 94·8; H, 5·2. Calc. for $C_{28}H_{18}$: C, 94·9; H, 5·1%). The acetic acid liquor from the above preparation contained diphenylmethane.

This *iso*dianthranyl is quite different from the colourless dianthranyl (m. p. above 360°) obtained by Barnett and Matthews (J., 1923, **123**, 380) by the reduction of anthrone, but is probably identical with the dianthranyl (m. p. 300°) described by Schulze (*Ber.*, 1885, **18**, 3034), Liebermann and Gimbel (*Ber.*, 1887, **20**, 1854) and Eckert and Hofmann (*Monatsh.*, 1915, **36**, 497). It is remarkable that neither Barnett and Matthews (*loc. cit.*) nor Schlenk (*Annalen* 1928, **463**, 165) has been able to obtain the product described by the above workers, although Schlenk (*loc. cit.*) obtained a dianthranyl m. p. 304°, by the action of sodiodiphenylmethane on 9-bromo anthracene. Schlenk's product is probably identical with tha described above, his analytical figures suggesting that his specime was not quite pure. He attributes the isomerism to the presenc of two different types of anthracene complex due to the non-coplana nature of the anthracene ring system (compare Bergmann an Mark, *Ber.*, 1929, **62**, 750).—SIR JOHN CASS TECHNICAL INSTITUT LONDON, *E.C.3.* [*Received, March 2nd, 1929.*]

Preparation of o-*Nitroacetophenone.* By WILLIAM OGILVY KEI MACK and JAMES FERGUS SMITH.

THE preparation of *o*-nitroacetophenone from ethyl *o*-nitrobenzoy acetoacetate (Needham and Perkin, J., 1904, **85**, 151) throug *o*-nitrobenzoylacetic acid is tedious, and the yield is unsatisfactor

o-Nitroacetophenone was obtained by Gevekoht (*Annalen*, 188 **221**, 323) by refluxing ethyl *o*-nitrobenzoylacetoacetate with fi times its volume of dilute sulphuric acid (1 part of concentrat acid and 2 parts of water), a small quantity of *o*-nitrobenzoylaceto being formed as a by-product.

In attempts to obtain *o*-nitroacetophenone by Gevekoht's meth 50%, 36%, and 28% (by weight) acid being used, the yields of *o*-nit

acetophenone and *o*-nitrobenzoylacetone were 27% and 52%, 22% and 68%, and 16% and 70%, respectively, of the theoretical. It would seem from the above that, when ethyl *o*-nitrobenzoylacetoacetate is heated with dilute sulphuric acid, hydrolysis of the ester group and elimination of carbon dioxide take place primarily; the acetyl group in the resulting *o*-nitrobenzoylacetone not being readily susceptible to hydrolysis, *o*-nitroacetophenone is not obtained to any great extent.

It was obviously essential to remove the acetyl group before hydrolysis of the ester group took place. This was achieved by refluxing for 7 hours an alcoholic solution of the ester containing 10% by weight of sulphuric acid, the acetyl group being removed as ethyl acetate. An amount of water equal to the volume of alcohol used was then added, and the whole distilled until the liquid had been reduced to its original volume; the ethyl acetate and the bulk of alcohol were thus removed. The residue was refluxed for about an hour and cooled, and the *o*-nitroacetophenone extracted in ether. The extract yielded practically nothing to dilute alkali solution, showing that very little, if any, *o*-nitrobenzoylacetone had been formed. The yield of *o*-nitroacetophenone (redistilled) exceeded 75% of the theoretical. Results almost as good were obtained when the fission of the acetyl group was carried out by a 50% aqueous-alcoholic solution containing 10% of sulphuric acid.

It is difficult to explain the fact that Gevekoht, using aqueous sulphuric acid, obtained *o*-nitroacetophenone as his main product. It is possible that some alcohol may have been present. The method here described, in which hydrolysis is carried out by alcoholic sulphuric acid, may prove of use in other cases where it is desired to eliminate an acetyl group without removal of a carboxyl group.

Part of the cost of the above experiments was defrayed by a grant from the Research Fund of the Chemical Society.—Research Laboratory, Royal College of Physicians, Edinburgh. [*Received, March 4th*, 1929.]

The Stability of Diazonium Salts of the Triazole Series. By Joseph Reilly and Denis Madden.

The rate of decomposition of diazonium salts of the pyrazole and pyrazolone series obeys approximately the unimolecular law (J., 1925, **127**, 2936). The decomposition of triazolediazonium salts is more rapid and at least two reactions are proceeding simultaneously. Substitution of alkyl groups tends towards stabilisation, which is also influenced by the nature of the alkyl group; *e.g.*, the *iso*butyl

derivative decomposes more slowly than the corresponding methyl-triazolediazonium salt under similar conditions. The nature of the anion and the amount of acid present also influence the stability. The comparative stability may be judged from the following table, which gives the c.c. of gas evolved from 0·002 g.-mol. of the various triazoles at 55° in presence of 6 mols. of acid.

	15 Mins.		30 Mins.	
	Nitrate.	Chloride.	Nitrate.	Chloride.
5-Amino-1 : 2 : 4-triazole	22·0	27·7	26·8	33·1
5-Amino-3-methyl-1 : 2 : 4-triazole...	19·5	22·1	23·2	28·4
5-Amino-3-ethyl-1 : 2 : 4-triazole ...	19·0	22·0	23·0	30·8
5-Amino-3-*iso*propyl-1 : 2 : 4-triazole	18·1	19·4	23·6	26·8
5-Amino-3-*iso*butyl-1 : 2 : 4-triazole	13·1	16·6	19·2	26·1

5-Amino-3-ethyl-1 : 2 : 4-triazole Nitrate.—Aminoguanidine nitrate (25 g.) was gently heated under reflux with 20 g. of propionic acid and a few c.c. of water for 24 hours. An aqueous solution of the product was made faintly alkaline with potassium carbonate and evaporated to dryness. An ethyl acetate extract of the residue, on treatment with concentrated nitric acid, yielded *5-amino-3-ethyl-1 : 2 : 4-triazole nitrate* (17 g.), m. p. 167° after recrystallisation from warm ethyl acetate–ethyl alcohol (Found: N, 40·15. $C_4H_8N_4,HNO_3$ requires N, 40·0%). The nitrate dissolved readily in hot water and hot ethyl alcohol.

5-Amino-3-ethyl-1 : 2 : 4-triazole crystallised from ethyl acetate had m. p. 152° (Found: N, 49·7. $C_4H_8N_4$ requires N, 50·0%).

3-Ethyl-1 : 2 : 4-triazole-5-azo-β-naphthylamine crystallised from ethyl alcohol in bright red needles, m. p. 259° after darkening at 242° (Found: N, 31·7. $C_{14}H_{14}N_6$ requires N, 31·6%). *3-Ethyl 1 : 2 : 4-triazole-5-azo-β-naphthol* crystallised from ethyl alcohol in orange-red needles, m. p. 180—181° (Found: N, 26·4. $C_{14}H_{13}ON$ requires N, 26·2%). *3-Ethyl-1 : 2 : 4 - triazole - 5 - azoacetylacetone* obtained as a yellow precipitate when sodium acetate was added to a solution of the diazonium salt and acetylacetone, melted at 236 after recrystallisation from ethyl alcohol (Found: N, 31· $C_9H_{13}O_2N_5$ requires N, 31·4%). *5-Diazo-3-ethyl-1 : 2 : 4-triazo chloroaurate* readily decomposed when heated (Found: Au, 45· $2C_4H_5N_5Cl_3Au,H_2O$ requires Au, 45·5%).

5-Amino-3-isobutyl-1 : 2 : 4-triazole nitrate, prepared by heatir 20 g. of *iso*valeric acid (b. p. 173—174°) and 20 g. of aminoguanidi nitrate for several hours, and isolated (16 g.) in the same way as t ethyl homologue, crystallised from hot ethyl acetate–ethyl alcoh in silvery needles, m. p. 171° (Found: N, 34·6. $C_6H_{12}N_4,HN$ requires N, 34·5%).—UNIVERSITY COLLEGE, CORK. [*Receive December 14th*, 1928.]

ANNUAL GENERAL MEETING,

HELD IN THE UNIVERSITY OF LEEDS

ON

THURSDAY, MARCH 21ST, 1929, AT 3.15 P.M.

THE President, Professor J. F. THORPE, C.B.E., D.Sc., F.R.S., was in the Chair.

The Report of the Council for 1928–1929, together with the Balance Sheets and Statements of Accounts for 1928, was presented. In the absence of the Treasurer, the PRESIDENT gave an account of the finances of the Society for the past year. The adoption of the report was proposed by Mr. Edward Hinks, seconded by Prof. C. K. Ingold, and carried.

REPORT OF COUNCIL, 1928–1929.

I. *Fellowship Statistics.*

IN the last Report of Council it was stated that the number of new Fellows elected during 1927 was 80 below the average for the last ten years, and that the total number of Fellows at the end of 1927 showed a decrease of 53 compared with the previous year. Concern at the position was expressed and an appeal made to Fellows to use their best endeavours to increase the membership. The Council has to report, however, that the diminution in membership has slightly increased this year.

At December 31st, 1927, the number of Fellows was 4040. During 1928, 203 Fellows were elected and 11 reinstated, making a gross total of 4254. The deaths recorded were 40, 135 Fellows resigned, and the names of 99 were removed for non-payment of annual subscriptions, as against 40, 103, and 110, respectively, the previous year. The losses, therefore, outnumber the elections by 60. The total number of Fellows at December 31st, 1928, was 3980, showing a decrease of 60.

While the number of Fellows removed under Bye-law IV is 11 less than last year, the resignations show an increase of 32. Notwithstanding an increase of 14 in the number of new Fellows, the elections still fall short by 68 of the average for the last ten years. The position causes anxiety and must be investigated by the Council.

The Society has suffered the loss by death of one of its distinguished Honorary Fellows, Professor Theodore W. Richards, who was elected in February, 1908. A memorial lecture in his honour is to be delivered before the Society by Sir Harold Hartley on April 25th. The number of Honorary Fellows at the end of 1928 was 22.

Jubilee Fellows.

The congratulations of the Society have been sent to Mr. Thomas Bolas, who, elected on March 18th, 1869, has completed his sixtieth year of Fellowship, and to the following, who have attained their Jubilee as Fellows :

Thomas Herbert Norton	April 4th, 1878.
William Arthur Harrison Naylor	April 4th, 1878.
Samuel Anthony Goldschmidt	April 4th, 1878.
Henry Russell Smith	May 16th, 1878.
William Jago	May 16th, 1878.
William Risdon Criper	June 20th, 1878.
George William Slatter........................	Dec. 5th, 1878.
John Isaac Watts	Dec. 5th, 1878.
William Stevenson	Feb. 6th, 1879.
Charles Frederick Cross	Feb. 6th, 1879.
Peter Phillips Bedson	Feb. 6th, 1879.

(Note : These appear in the order of election.)

II. *Journal.*

The Journal for 1928 contains 3308 pages, of which 3216½ pages are occupied by 438 memoirs (a record number) and 28 notes, the remaining 91½ pages being devoted to Obituary Notices (31 pages), two Lectures (38½ pages), and the Report of the Annual General Meeting and the Presidential Address (22 pages). The volume for 1927 contains 414 memoirs and 28 notes, occupying 3096 pages.

During 1928, 501 papers were offered to the Society for publication in the Journal; of these, 15 were declined. The corresponding numbers for 1927 are 485 and 23. The average interval between the dates of receipt and of publication of papers is 10·75 weeks for 1928 and 10·5 weeks for 1927.

The Council records its indebtedness to Fellows and others for their services to the Society in refereeing papers.

III. *Abstracts.*

The " A " Abstracts for 1928 contained 9456 abstracts occupying 1408 pages, compared with the corresponding figures in 1927 of 8010 and 1230, respectively. These comprised 4718 in General, Physical, and Inorganic Chemistry, 224 in Geochemistry, 2236 in Organic Chemistry, and 2268 in Biochemistry. The corresponding figures for 1927 were 4157, 80, 2095, and 1678.

The increase, amounting to about 18 per cent., in the number of abstracts in the " A " Section is noteworthy. This is due to the greater amount of chemical literature published, and not to a general widening of scope of the subject matter abstracted. The average length of the abstracts was 0·30 of a column, the same as for 1927; and the Bureau considers that this average cannot usefully

be reduced. The cost per page has been reduced by more than two shillings following the adoption of the lighter paper for 1928.

Index. The Joint Annual Index for the Abstracts for 1927 covered 514 pages, as compared with 430 pages for the 1926 Index. The cost of printing the Index was £1135 7*s*. 8*d*. and of the paper £247 8*s*. 1*d*. The printing of the 1928 Index has been entrusted to Messrs. Clay & Sons. It is satisfactory to note that the cost of setting the type has been reduced by 10 per cent.

Status. The Bureau submitted a report on this matter to the Councils of the two Societies suggesting that provision should be made for regularising the Bureau as a joint Committee. The Societies agreed to make such alterations in their respective Bye-laws as were necessary for this purpose.

Collective Index. The Bureau is considering the question of issuing a collective index to the Abstracts covering the period from 1923, and hopes to submit a report on the subject in due course.

IV. *Library.*

Excluding the evenings on which meetings of the Chemical Society were held, there were 8037 attendances during the past year as compared with 8002 in 1927. Of these, 5368 were made by Fellows of the Chemical Society, while 2669 were made by Members of Contributing Societies, as against 2594 in 1927. The number of books borrowed during 1928 was 5262, as against 5489 the previous year. Of these, 1337 were issued by post, as against 1381 in the preceding year.

The additions to the Library comprise 281 books, of which 85 were presented, 664 volumes of periodicals and 138 pamphlets, as against 286 books, 625 volumes of periodicals and 86 pamphlets last year. The total number of volumes added during the year was 945, showing an increase of 34. The Library now contains 32,832 volumes, consisting of 9,928 books and 22,904 bound volumes of periodicals.

The Council expresses its gratitude to all those who have presented volumes to the Library during the year.

V. *General.*

The Arrhenius Memorial Lecture was delivered by Sir James Walker at the Royal Institution on Thursday, May 10th, and was published in the Journal (p. 1380). The first of the Liversidge Lectures, founded in accordance with the will of the late Professor Archibald Liversidge, was delivered on November 29th by Professor F. G. Donnan, who chose as his subject " Physical Chemistry in the

Service of Biology." Professor W. H. Perkin will deliver the first Pedler Lecture on May 30th, 1929, his subject being "The Early History of the Synthesis of Closed Carbon Chains."

It was decided, as an experiment, to hold the Ordinary Scientific Meetings during May and June at 5.30 p.m. It was subsequently agreed that the meetings in the Session 1928–1929 should be held at the usual hour of 8 o'clock.

The President represented the Society at the Celebrations in Madrid of the 25th Anniversary of the Sociedad Española di Fisica y Quimica, and presented an address of congratulation. The President was present at the luncheon given by the Faraday Society on November 9th, when its 25th Anniversary was celebrated, and at the Hauptversammlung of the Deutsche Bunsen Gesellschaft held in Munich in May. He also attended the Liebig–Wöhler Celebrations at Darmstadt and Giessen on July 7th and 8th, presenting on behalf of the Society an address of congratulation. The Council sent for exhibition at the Liebig–Wöhler Celebrations the portrait of Baron von Liebig presented to the Society by Mrs. Alec Tweedie, and has received the thanks of the German Chemical Society for the loan. A copy of the portrait, executed by Mr. G. A. Pownall, the cost of which has been met by private subscription, will be presented on behalf of the Council and Fellows to the German Chemical Society which has expressed its willingness to receive the gift and its appreciation of the spirit which prompted the offer.

Professor C. S. Gibson represented the Society at the Anniversary Dinner in Paris of the Société Chimique de France on June 2nd and at the Celebrations of the 25th Anniversary of the Nederlandsche Chemische Vereeniging held at The Hague in July. Professor W. P. Wynne was present as the Society's delegate at the opening of the New Research Laboratories of the Safety in Mines Research Board at Sheffield on October 11th, and an address of congratulation was sent to the President and Members of the Mendeléeff Congress at Kazan in honour of the centenary of Butleroff.

Professor G. Barger and Professor H. Bassett have been appointed to serve on the Organic and Inorganic Nomenclature Committees respectively, of the International Union.

At the Anniversary Dinner of the Society held on March 22nd the Society was honoured by the presence of many distinguished guests, including the President of the International Union of Pure and Applied Chemistry, the Presidents of the Finnish, Swedish, and Swiss Chemical Societies, and the Ministers for Finland and Switzerland. The Council has decided that the Annual General Meeting and Anniversary Dinner for 1929 shall be held in Leeds on March 21st. A local Committee has been formed to carry out arrang

ments, of which Mr. H. S. Patterson has agreed to act as Hon. Secretary.

The Society was represented on the Bureau of Chemical Abstracts by Professor C. S. Gibson, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Professor G. T. Morgan, and the Treasurer, and on the Federal Council of Pure and Applied Chemistry by the President, Professor C. S. Gibson, and Sir William J. Pope.

The financial arrangements made in 1923 regarding the *Journal of Physical Chemistry* came to an end on December 31st, 1928. The Council was informed in June that the Chemical Foundation had agreed to subscribe towards the cost of publication the sum of $5,000 annually for four years as from January 1st, 1929, thus enabling the Editorial Board to continue publishing the Journal as heretofore. Professor James Kendall has been appointed to represent the Society on the British Editorial Board in the place of Dr. T. Slater Price, who has retired. During 1928, the British members of the Editorial Board received 19 papers, of which 7 have been published, 8 await publication, 2 are under consideration, and 2 have been declined. Fifteen reviews of books have also been prepared.

The Society has received from Professor H. E. Armstrong a photograph of a group of chemists; from Professor H. B. Dixon a photograph of a group of chemists taken on the occasion of the British Association Meeting in Oxford in 1894; from Lady Tilden various framed photographs; and from Miss Florence E. Watts an engraving of Mendeléeff, formerly the property of the late Sir Edward Thorpe; also from Dr. O. Rosenheim two manuscript letters by Baron von Liebig, and from Mr. F. W. Hodges two manuscript letters by Bunsen and Faraday. The collection of Medals has been increased by the Liebig–Wöhler Medals received from the President, the Scheele and Berzelius Medals from Miss Florence E. Watts, and the Pasteur Medal from Dr. E. W. Maddison. The Society has also received gifts of its publications from Professor G. G. Henderson and Mr. J. I. Watts. The Council has expressed its thanks to these donors.

Volume XXV of the Annual Reports (1928), besides dealing with the usual subjects, contains a special report on Catalysis. The subject of Stereochemistry has been dealt with sectionally instead of being written by one Reporter as was done last year.

The publication of a list of Physico-Chemical Symbols has been considered, and it has been decided to take no action pending the receipt of a report from the International Union, which has agreed to consider the matter at the first favourable opportunity. The question of preparing a Table of Atomic Weights has also been

undertaken by a special committee, and a Table, together with a report containing a reasoned statement for the accepted values, has been published in the Journal (January, 1929). This table was included in Vol. XXV of the Annual Reports and is also published separately on cards which can be obtained from the Assistant Secretary (price 2*d*. each, or 1*s*. 6*d*. per dozen).

As stated in the last Report of Council, the question of revising the Bye-Laws was referred to a Committee. The final report of this Committee was received and adopted by the Council on June 21st, and at an Extraordinary General Meeting on October 18th, the alterations and additions proposed were approved. The revised Bye-Laws were issued to Fellows in January, 1929, and a brief explanation of the significance of the alterations and additions appeared in the Proceedings for October.

The first of the volumes of special lectures which have been delivered before the Society since its foundation in 1841 contained the Faraday Lectures given between 1869 and 1927. It was published in October, and can be obtained by Fellows at 5*s*. 6*d*., post free. Fellows are reminded that this Volume, which can also be obtained in paper covers, and Volumes I and II of the Memorial Lectures (price 9*s*. and 7*s*. each, respectively) are suitable for presentation as prizes.

The Annual Chemical Dinner, in which the Society co-operated, was held on Friday, November 9th, the principal guest of the evening being the Rt. Hon. W. G. A. Ormsby-Gore, M.P., Under-Secretary of State for the Colonies. There was present a large and representative gathering of chemists.

The Chemical Club, the members of which dine together at 6.30 p.m. on Council meeting days, has met nine times during 1928.

At the Ordinary Scientific Meeting on June 21st, the President made a presentation to Mr. F. W. Clifford of two cheques, one from the Council and one from Fellows, together with a clock, and a book containing the signatures of those Fellows who had contributed, to mark the completion of his 25th year as Librarian.

The Council records its thanks to those who have delivered lectures before the Society, to Fellows and others who have prepared obituary notices, to the authors of the Annual Reports for 1928, and to the Committee on Atomic Weights.

VI. *Research Fund.*

Sixty-one applications for Research Grants were received from Fellows during 1928, asking for £719 10*s*. and two from non-Fellows asking for £29 10*s*. Grants amounting to £626 in all were awarded

VII. *Financial.*

This year the Accounts appear in a somewhat simplified form compared with that adopted in previous years. All income and expenditure on account of the publications of the Society have been transferred to the Publications Fund Account, from which it can now be seen at once what has been the gross and net cost to the Society of the publications for the past year.

The Income of the Society has decreased by £126 0*s*. 8*d*., and the expenditure has increased by £75 8*s*. 4*d*.

General Purposes Account. The main causes for the decreased income are to be found in the Annual Subscriptions, which are £81 8*s*. less, and in the investments, which have yielded £43 12*s*. 3*d*. less.

The Administration Expenses are less by £49 11*s*. 9*d*. There are slight increases in salaries and wages, amounting to £26 0*s*. 11*d*. and £50 has been spent in the preparation of an inventory. There is a saving of £68 18*s*. 4*d*. on house expenses, coal, and furniture, and of £14 8*s*. 8*d*. on postages, miscellaneous printing and stationery. The sum transferred to Publications Fund Account to meet the cost of publications is £112 1*s*. 10*d*. in excess of that last year and the contribution to the Library is greater by £49 8*s*.

Publications Fund Account. Disregarding in the income account the sums of £3217 18*s*. 7*d*. for 1927 and £220 3*s*. 11*d*. for 1928, which have been capitalised, and the sums transferred from General Purposes Account, the income for 1928 exceeds that for 1927 by £27 7*s*. 7*d*. The sales of publications and income from advertisements show an increase of £120 10*s*. 9*d*.; on the other hand, the investments yielded £73 15*s*. 2*d*. less.

Journal. The total expenditure on account of the Journal shows a decrease of £135 11*s*. 6*d*. compared with that of the previous year. The expenditure on account of printing the Journal for 1928 is increased by £83 19*s*. 10*d*., due to there being 212 more pages than in 1927. The cost of paper was £544 9*s*. 7*d*. as against £701 18*s*. 5*d*. in 1927; the saving of £157 10*s*. 10*d*. has been due to the use of a lighter paper.

Abstracts. The Abstracts this year have cost £384 10*s*. 11*d*. more than in 1927. Abstractors' Fees account for £179 10*s*. 1*d*. of this. The charge for printing is up by £196, owing to an increase of 178 in the number of pages. The expenditure of £629 14*s*. 7*d*. on paper in 1928, as against £565 7*s*. 0*d*. in 1927, covers fifteen months' supply. The cost of the paper actually used in the Abstracts (including Index) was approximately £468, so that the introduction of the lighter paper has meant a saving of about £97, in spite of the increase in the number of pages.

Distribution. The measure of economy adopted by the Counci in using a lighter paper has also enabled a saving of £212 6*s.* 5*d.* t be *made in* distribution charges for the Journal and Abstracts.

Library. The donations received from contributing Societie exceed those for the previous year by £10 10*s.*, but owing to a increase in the sum spent on books and binding, the contributio from the general funds of the Society is £49 8*s.* more than in 1927

Income Tax. In the last Report of Council, it was stated tha the Board of Inland Revenue was unable to refund Income Tax pai on the Society's investments pending the decision of the High Cour on two societies chosen as test cases. These cases were heard i June and decisions were given against the two Societies concerned The Council is glad to report, however, that as a result of energeti representations, both in writing and personal interview, made b the President, the Treasurer, and Mr. W. B. Keen, the Council ha been informed by the Board of Inland Revenue that the claim o the Chemical Society for exemption from Income Tax as a bod established for charitable purposes only has been admitted.

General. A contribution of £50 has been made towards th expenses of the Federal Council for 1928, £10 to the Sevent International Congress of Photography, and £5 to the Ne International Association for Testing Materials.

The thanks of the Council have been conveyed to the Roya Society for the sum of £350 received from the Government Public ations Grant towards the cost of the Society's publications for 1928 The Council is also gratified to report that it received during th year a donation of £100 to the Publications Fund from Imperia Chemical Industries, Ltd.

The insurances on the fixtures, fittings, and books in the Society' rooms have been carefully revised and the necessary alteration made.

The Council has decided that the Society shall act as its own Publisher as from January 1st, 1929. The Council takes this opportunity of expressing its appreciation of the services rendered to the Society by Messrs. Gurney & Jackson, who have acted as its Publishers for many years.

A vote of thanks to the Auditors (Dr. G. W. Monier-Williams, Dr. O. L. Brady, and Dr. A. E. Dunstan), which was proposed by Mr. M. P. Applebey, and seconded by Dr. H. McCombie, was carried. On the proposal of Prof. J. W. Cobb, seconded by Prof. A. Findlay, Dr. O. L. Brady, Dr. A. E. Dunstan, and Dr. P. Haas were elected Auditors to audit the Accounts of the Society for 1929.

Prof. W. P. Wynne proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council and Committees for their services during the past year. This, which was seconded by Mr. F. P. Dunn, and carried, was acknowledged by Prof. R. Robinson.

The report on the election to vacancies on the Council for the year 1929—1930 was read as follows :

Vice-President who has filled the office of President.—W. P. Wynne.

Vice-Presidents who have not filled the office of President.—T. A. Henry and Emile S. Mond.

Ordinary Members of Council (Country Members).—G. M. Bennett, J. A. Cranston, W. E. Garner, and J. I. O. Masson.

A vote of thanks to the Scrutators (Mr. W. M. Colles and Mr. D. C. Jones) was proposed by Prof. F. M. Rowe, seconded by Prof. C. S. Gibson and carried.

After tea, the company reassembled in the Great Hall of the University, where the Society was officially welcomed by the Vice-Chancellor, Dr. J. B. Baillie, and by the Lord Mayor of Leeds. The President then delivered his Address, entitled " Co-operation in Science and Industry." A vote of thanks to the President for his services in the Chair during the past year and for his Address was proposed by Prof. W. H. Perkin and seconded by Sir Robert Robertson. This was carried with acclamation and the President acknowledged it.

INCOME AND EXPENDITURE GENERAL PU

1927 £	s.	d.	£	s.	d.	*Income.*	19 £	s.	d.	
			175	10	0	To Life Compositions				
						,, Annual Subscriptions :—				
942	6	0				Received in advance, on account of 1928	912	0	0	
8397	3	0				,, during 1928 ,, ,, ...	8313	0	0	
524	0	0				,, ,, ,, ,, 1927	563	17	0	
45	2	0				,, ,, ,, ,, 1926 and previous years	39	0	0	
9909	5	0					9827	17	0	
500	0	0				*Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	500	0	0	
9409	5	0					9327	17	0	
500	0	0				*Add* Arrears at date: £894; Estimated to realise as per Balance Sheet	500	0	0	
			9909	5	0					9
						,, Investments, Dividends on :—				
25	3	10				£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	25	3	10	
36	10	0				£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock, 1914/54	36	10	0	
31	10	0				£1400 India 2½ per cent. Stock	26	0	0	
48	0	0				£2400 Bristol Corporation 2½ per cent. Debenture Stock	48	0	0	
86	16	4				£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	86	16	4	
28	16	0				£1200 Leeds Corporation 3 per cent. Stock	28	16	0	
40	10	0				£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	36	0	0	
28	16	0				£1200 London and North Eastern Railway 3 per cent. Debenture Stock	28	16	0	
19	12	0				£700 Canada 3½ per cent. Stock, 1930/50	19	12	0	
105	0	0				£2100 5 per cent. War Stock, 1929/47	105	0	0	
44	0	0				£1100 5 per cent. War Bonds, 1929/47	44	0	0	
21	12	0				£600 Funding Loan, 4 per cent., 1960/90	19	4	0	
332	9	0				£11212 9*s.* 3½ per cent. Conversion Stock	323	4	0	
			848	15	2					
			69	15	3	,, Income Tax recovered				
			92	15	3	,, Income Tax recoverable				
			66	12	10	,, Interest on Deposit				
			48	17	0	,, Miscellaneous Receipts				
						,, Editing Liversidge Papers (see contra)				
			£11,211	10	6					£11

£	s.	d.	
102	7	10	To Pedler Bequest, Balance of Income from Residue of Estate of Sir Alexander Pedler ... ...
2985	*16*	*2*	,, *Pedler Bequest, Balance of Capital ... ...
£3,088	*4*	*0*	

* *Legacy Duty amounted to £336 1s.*

OUNT FOR THE YEAR ENDED 31ST DECEMBER 1928.

1927 s.	d.	£	s.	d.	*Expenditure.*	1928 £	s.	d.	£	s.
					By Administration Expenses:—					
2	0				Salaries of Staff	1456	7	11		
17	6				Wages (Commissionaire, Housekeeper, and Charwomen)	290	12	6		
12	11				Coal and Lighting	51	2	8		
19	5				House Expenses and Repairs	116	10	4		
12	6				Furniture	19	13	6		
9	5				Telephone	18	8	1		
5	0				Insurances	15	2	5		
10	0				Accountants' Charges	31	10	0		
0	0				Ditto Pedler Bequest	—				
9	9				Commission on Recovery of Income Tax (Estd.) ...	8	0	0		
9	2				Miscellaneous Printing and Stationery	279	19	7		
14	5				Postages	163	15	4		
0	1				Superannuation of Staff	128	9	10		
18	0				Addresses	15	6	6		
3	2				Miscellaneous Expenses	80	12	11		
-					Preparation of Inventory and Valuation for Insurance	50	0	0		
		2775	3	4					2725	11
		133	17	1	,, Expenses of Meetings				121	14
		92	17	11	,, Advance Proofs and Reports of Meetings				99	11
					,, Donations:—					
0	0				Federal Council	50	0	0		
-					*International Congress of Photography*	10	0	0		
-					International Testing Association	5	0	0		
		100	0	0					65	0
		5695	15	0	,, Contribution to Publications Fund				5807	16
		175	10	0	,, Transfer to ditto (Life Composition Fees)				60	0
		1636	0	6	,, *Contribution to Library*				1885	8
		146	0	0	,, Transfer to Staff Pensions Fund				150	0
		—			,, Editing Liversidge Papers (see contra)				100	0
		456	6	8	,, Excess of Ordinary Income over Ordinary Expenditure carried to Balance Sheet				264	17
		£11,211	10	6					£11,069	19

102	7	10	By Publications Fund—Income from Pedler Bequest	—
2985	16	2	,, Publications Fund—Capital from Pedler Bequest	—
£3,088	4	0		

1927 £ s. d.	1927 £ s. d.	*Income.*	1928 £ s. d.	1928 £ s. d.
		To Publication Sales :—		
2763 11 11		Journals and Proceedings ...	2751 13 2	
2336 2 2		Abstracts	2431 2 1	
118 5 5		Collective Index, Vols. I–VI ...	87 3 7	
820 19 8		Annual Reports on Progress of Chemistry	833 18 10	
15 8 3		Memorial Lectures. Vol. II. ...	—	
9 6		Other Publications	12 6	
6056 16 11			6104 10 2	
543 16 4		*Less* Publishers' Commission ...	547 19 5	
	5513 0 7			5556 10 9
548 12 9		,, Proceeds of Advertisements in Journal and Abstracts	672 18 8	
153 14 1		*Less* Commission	200 19 5	
	394 18 8			471 19 3
	175 10 0	,, To Transfer from General Purposes Account, being Life Composition Fees for year ...		60 0 0
	85 3 6	,, Subscriptions		65 15 6
	25 0 0	,, *Donations*		100 0 0
	350 0 0	,, Government Publications Grant (through the Royal Society) ...		350 0 0
168 9 0		,, Dividend on £6141 15s. 6d. Conversion Stock, 3½ per cent. ...	169 1 1	
153 19 2		,, Ditto £3079 3s. 9d. War Stock, 5%, 1929/47	153 19 2	
71 0 0		,, Ditto £817 P. & O. Steam Navigation Co. Deferred Shares ...	94 2 4	
7 13 5		,, *Ditto 186 £1 Shares Langla (Sylhet) Tea Co.*	10 18 1	
25 5 3		,, Ditto 124 £1 Shares Nedeem Tea Co.	38 17 3	
102 7 10		,, Balance of Income from Pedler Bequest, transferred from General Purposes Account	—	
3 3 6		,, Interest on Deposit	1 5 1	
	531 18 2			458 3 0
13 3 5		,, Income Tax recovered (*Net*) ...	—	—
18 9 0		,, Income Tax recoverable (Net) ...	—	60 3 11
	31 12 5			
	2985 16 2	,, Balance of Capital from Pedler Bequest, transferred from General Purposes Account ...		—
		,, Transfer from General Purposes Account (the balance of ex-		

1927 £ s. d.	1927 £ s. d.	*Expenditure.*	1928 £ s. d.	1928 £ s. d.
		By Expenses on account of Journal :—		
1020 15 0		Editorial Salaries	1036 11 8	
63 15 11		Editorial Postages	63 19 3	
3635 14 6		Printing of Journal	3562 3 6	
85 18 3		Banding	82 19 8	
77 16 6		Printing of Advertisements ...	86 14 4	
5 3 5		Addressograph Labels	3 14 6	
529 7 0		*Distribution of Journal*	423 3 10	
320 11 9		Authors' Copies	331 0 7	
5 5 0		Insurances	5 18 2	
—		Warehousing of Stock	1 1 5	
37 16 3		Superannuation of Staff	37 16 3	
10 13 3		Miscellaneous	22 2 2	
	5792 16 10			5657 5 4
		,, Expenses on account of Abstracts :—		
1100 17 11		Editorial Salaries (Bureau) ...	1131 3 10	
44 5 9		*Editorial Postages (Bureau)* ...	38 7 7	
1162 17 7		Abstractors' Fees (Bureau) ...	1342 7 8	
2395 7 4		Printing of Abstracts (Bureau £464 16s. 0d.)...	2671 19 9	
665 13 8		Index (Bureau—Printing £543 6s. 3d., Paper £106 2s. 7d.) ...	649 8 10	
85 18 2		Banding (Bureau £2 13s. 5d.) ...	82 19 8	
5 3 5		Addressograph Labels	3 14 5	
529 7 1		Distribution of Abstracts (*Bureau £16 2s. 11d.*)	423 3 10	
5 5 0		Insurances	5 3 2	
—		Warehousing of Stock	1 1 6	
9 4 5		Superannuation of Staff	9 4 5	
41 4 6		Miscellaneous (Bureau)	71 1 1	
	6045 4 10			6429 15 9
	587 19 7	,, Annual Reports on the Progress of Chemistry		612 6 4
	9 12 6	,, Purchase of Back Numbers of *Publications*		10 17 11
	129 8 2	,, List of Fellows—Printing, etc. ...		—
	6 1 0	,, Subscriptions in advance (carried forward)		—
		,, Carried to balance sheet of Publications Fund, viz. :—		
175 10 0		,, Life Composition Fees	60 0 0	
13 3 5		,, Income Tax recovered (Net) ...	—	
18 9 0		,, Income Tax recoverable (Net) ...	60 3 11	
25 0 0		,, *Donations*	100 0 0	
2985 16 2		,, Balance of Capital from Pedler Bequest	—	
				220 3 11

1927 £ s. d.	1927 £ s. d.	Income.	1928 £ s. d.	1928 £ s. d.
		To Dividends on :—		
32 0 0		£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	32 0 0	
20 13 8		£1034 Great Western Railway 2½ per cent. Stock	20 15 6	
30 7 2		£1142 16s. New South Wales 3 per cent. Stock	27 8 8	
30 5 11		£1122 Metropolitan Water Board 3 per cent. "B" Stock	26 18 8	
27 5 10		£1483 London, Midland and Scottish Railway 4 per cent. Debenture Stock	47 9 0	
19 6 10		£806 Victoria 3 per cent. Stock, 1929/49	19 6 10	
221 18 6		£4498 11s. 0d. 5% War Loan, 1929/47	224 18 6	
163 3 8	548 1 7	£5164 13s. 9d. 3½% Conversion Stock	144 12 2	543 7 6
	12 8 3	,, Income Tax recovered		—
	12 8 3	,, Income Tax recoverable		49 13 9
	137 18 0	,, Repayment of Grants		141 8 9
	8 7 7	,, Interest on Deposit		2 16 9
	1 15 4	,, Sale of Apparatus		—
	5 3 11	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		—
	£726 2 11			£737 6 9

1927 £ s. d.	Expenditure.	1928 £ s. d.
697 10 0	By Grants	618 0 0
12 5	,, Commission on Recovery of Income Tax	3 2 1
20 0 0	,, Honorarium to Lecturer	—
2 0 0	,, Cost of Medal	—
—	,, Stationery	11 14 9
6 0 6	,, Miscellaneous Expenses	6 2 6
—	,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet	98 7 5
£726 2 11		£737 6 9

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

1927 £ s. d.	1927 £ s. d.		1928 £ s. d.	1928 £ s. d.
		To Dividends on :—		
25 0 0		£500 National War Bonds, 5%, 1929...	25 0 0	
25 0 0		£527 10s. Treasury Bonds, 5%, 1933/35	21 0 7	
2 3 2		£61 15s. 8d. Conversion Stock, 3½%	2 3 2	
1 13 5	53 16 7	Interest on Deposit	2 7 11	50 11 8
	102 18 5	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		—
	£156 15 0			£50 11 8

1927 £ s. d.		1928 £ s. d.
6 15 0	By Cost of Plaque	—
150 0 0	,, Prize	—
—	,, Balance being excess of Income over Expenditure carried to Balance Sheet	50 11 8
£156 15 0		£50 11 8

1927 £ s. d.	1927 £ s. d.	Income.	1928 £ s. d.	1928 £ s. d.
		To Donations:—		
		Association of British Chemical		
[illegible] 0 0		Manufacturers	150 0 0	
[illegible] 10 0		Biochemical Society	10 10 0	
[illegible] 5 0		Faraday Society	5 5 0	
[illegible] 0 0		Institute of Brewing	45 0 0	
[illegible] 0 0		Institute of Chemistry ...	250 0 0	
[illegible] 0 0		Society of Chemical Industry ...	100 0 0	
[illegible] 10 0		Society of Dyers and Colourists	10 10 0	
[illegible] 10 0		Society of Public Analysts ...	21 0 0	
	581 15 0			592 5 0
	—	,, Miscellaneous receipts		10 7 7
		,, Contribution from General Purposes		
	1636 0 6	Account		1685 8 6
	£2217 15 6			£2288 1 1

1927 £ s. d.	Expenditure.	1928 £ s. d.
1295 10 0	By Salaries and Wages	1294 9 0
92 11 9	,, Superannuation Premium for Library Staff	92 15 0
491 18 7	,, Books and Periodicals	589 14 0
140 15 9	,, Binding	151 14 5
73 11 0	,, Printing, Stationery and Postage	72 15 0
105 9 5	,, Lighting, Heating, Furniture Insurance, etc.	76 3 10
17 19 0	,, Miscellaneous	10 9 10
£2217 15 6		£2288 1 1

STAFF PENSIONS FUND.

1927 £ s. d.		1928 £ s. d.	1928 £ s. d.
146 0 0	To Transfer from General Purposes Account ...		150 0 0
5 5 0	,, Donations		—
—	,, Interest on Deposit		2 12 0
	Dividends on:—		
18 11 10	,, £371 17s. 1d. War Loan, 5%, 1929/47 ...	18 11 10	
—	£289 4s. 4d. Conversion Stock, 3½% ...	4 1 0	
			22 12 10
£169 16 10			£175 4 10

1927 £ s. d.		1928 £ s. d.
146 0 0	By Pensions paid during 1928	136 0 0
	,, Excess of Income over Expenditure carried to Balance	
23 16 10	Sheet	39 4 10
£169 16 10		£175 4 10

SPECIAL PUBLICATIONS FUND.

1927 £ s. d.	1927 £ s. d.		1928 £ s. d.	1928 £ s. d.
		To Sales of Publications:—		
		Abstracts "A" printed on one side		
—		of the paper	28 0 0	
34 5 0		Memorial Lectures, Vol. I.	27 4 0	
—		Do. Vol. II.	24 4 0	
44 1 10		Portraits	9 2 11	
3 1 3		Faraday Lectures	13 17 4	
81 8 1			102 8 3	
6 4 4		Less Commission	4 10 6	
	75 3 9			97 17 9
		,, Dividend on £2115 8s. 10d. Conver-		
	59 4 8	sion Stock, 3½%		56 4 8
	3 8 10	,, Interest on Deposit		5 5 3
	7 8 0	,, Income Tax recovered		—
				14 16 0

1927 £ s. d.		1928 £ s. d.
	By Cost of Reproduction:—	
4 15 6	Faraday Lectures	275 1 3
—	Memorial Lectures, Vol. II.	130 0 0
3 3 0	,, Advertising	—
—	,, Reprints for Memorial Lectures, Vol. III.	6 3
	,, Production of Abstracts "A" printed on one side of the	
—	paper	43 1 6
7 5	,, Commission on recovery of Income Tax	—
—	,, Commission on Income Tax recoverable	1 2 2
	,, Excess of Income over Expenditure carried to Balance	
144 7 4	Sheet	—

Income.	1928 £ s. d.	*Expenditure.*	1928 £ s. d.
To Dividend on £1299 9s. 4d. Conversion Loan, 3½% (half year)	18 3 10	By Honorarium, Liversidge Lecturer	21 0 0
,, Interest on Deposit	4 4 4	,, Excess of Income over Expenditure carried to Balance Sheet	1 8 2
	£22 8 2		£22 8 2

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1928.

GENERAL PURPOSES.

1927 £ s. d.	1927 £ s. d.	*Liabilities.*	1928 £ s. d.	1928 £ s. d.
		To Subs. received in advance:—		
	912 0 0	At £3		960 0 0
	2,350 10 1	,, Sundry Creditors (Printing and other Expenses)		2,108 19 11
	78 15 3	,, Bankers—overdraft ...		374 6 7
25,840 10 8		,, Excess of Assets over Liabilities as per last Balance Sheet ...	26,296 17 4	
456 6 8		*Add* Excess of Income over Expenditure for Year	254 17 8	
	26,296 17 4		26,551 15 0	
		Deduct Transfers to Special Funds:— Staff Pension Fund ... ... £200; Special Lectures Fund £500	700 0 0	
				25,851 15 0
	£20,635 2 8			£29,301 1 6

1927 £ s. d.	*Assets.*	1928 £ s. d.	1928 £ s. d.
	By Investments (value when acquired):—		
839 3 7	£787 London, Midland and Scottish Railway 4% Debenture Stock ...	839 3 7	
1650 0 0	£1520 14s. 3d. Cardiff Corp. 3% Stock	1650 0 0	
1316 1 0	£1400 India 2½ per cent. Stock ...	1316 1 0	
2070 2 0	£2400 Bristol Corpn. 2½% Debenture Stock, Bristol Dock Account ...	2070 2 0	
3572 0 4	£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
1143 1 0	£1200 Leeds Corporation 3% Stock	1143 1 0	
1460 13 6	£1500 Transvaal 3 per cent. Guaranteed Stock, 1923–53	1460 13 6	
1033 11 0	£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0	
704 8 6	£700 Canada 3½% Stock, 1930/50 ...	704 8 6	
1995 0 0	£2100 5 per cent. War Stock, 1929/47	1995 0 0	
1045 0 2	£1100 5% National War Bonds, 1929/47	1045 0 2	
480 0 0	£600 4 per cent. Funding Loan, 1960/90	480 0 0	
8987 2 2	£11,212 9s. 3½ per cent. Conversion Stock	8487 2 2	
	(Market Value £21,012 1s. 6d.)		25,796 3 3
26,296 3 3			
2827 9 11	,, Sundry Debtors		3,003 5 7
500 0 0	,, Subscriptions in Arrear, £894. Estimated to realise		500 0 0
11 9 6	,, Cash in Hand		2 12 8
£29,685 2 8			£29,301 1 6

PUBLICATIONS FUND.

1927 £ s. d.	1927 £ s. d.	Liabilities.	1928 £ s. d.	1928 £ s. d.
	—	To Sundry Creditors ...		26 12 9
	6 1 0	,, Subscriptions received in advance		—
9157 1 9		,, Excess of Assets over Liabilities as per last Balance Sheet	10,375 0 4	
1217 18 7	10,375 0 4	*Add* Amount transferred from Income and Expenditure Account for Investment	220 3 11	10,595 4 3
	£10,381 1 4			£10,621 17 0

1927 £ s. d.	Assets.	1928 £ s. d.	1928 £ s. d.
	By Investments (value when acquired):—		
4500 0 0	£6141 15*s*. 6*d*. 3½% Conversion Stock	4663 10 0	
3100 0 0	£3079 3*s*. 9*d*. 5% War Stock 1929/47	3100 0 0	
1846 0 0	£817 P. & O. Steam Navigation Co. Deferred Stock	2060 0 0	
290 12 6	186 Ordinary Shares (£1) Lungla (Sylhet) Tea Co.	290 12 6	
403 0 0	124 Ordinary Shares (£1) Nedeem Tea Co.	403 0 0	
10,139 12 6	(Market Value £11,078 19*s*. 5*d*.)		10,517 2 6
64 4 0	,, Paid up on £107 P. & O. Steam Navigation Deferred Stock		—
18 9 0	,, Sundry Debtors		82 15 8
158 15 10	,, Cash at Bank		21 18 10
£10,381 1 4			£10,621 17 0

RESEARCH FUND.

1927 £ s. d.	1927 £ s. d.	Liabilities.	1928 £ s. d.	1928 £ s. d.
		To Sundry Creditors ...		2 9 8
14,471 16 3		,, Excess of Assets over Liabilities as per last Balance Sheet	14,466 12 4	
—		*Add* Excess of Income over Expenditure for Year	98 7 5	
5 3 11	14,466 12 4	*Less* Excess of Expenditure over Income for Year ...	—	14,564 19 9
				£14,567 9 5

1927 £ s. d.	Assets.	1928 £ s. d.	1928 £ s. d.
	By Investments (value when acquired):—		
1010 0 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
1049 15 11	£1034 Gt. West. Rly. 2½% Debentures	1049 15 11	
1000 0 0	£1142 16*s*. New South Wales 3 per cent. Stock, 1935	1000 0 0	
1002 16 9	£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
1508 3 6	£1483 London, Midland and Scottish Railway 4% Debenture Stock ...	1508 3 6	
706 6 2	£806 Victoria 3% Stock, 1929/49 ...	706 6 2	
4267 4 10	£4498 11*s*. 5% War Stock, 1929/47	4267 4 10	
3898 14 10	£5164 13*s*. 9*d*. 3½% Conversion Stock	3898 14 10	
14,443 2 0	(Market Value £13,476 10*s*. 0*d*.)		14,443 2 0
12 8 3	,, Sundry Debtors		49 13 9
11 2 1	,, Cash at Bank, Current Account ...		74 13 8
£14,466 12 4			£14,567 9 5

102 18 5		*Less* Excess of Expenditure over Income for Year ...	—		50 1 5	£61 15s. 8d. 3½% Conversion Stock ... (Market Value £1106 14s. 9d.)	50 1 5	1050 1 5
—		*Add* Excess of Income over Expenditure for year ...	50 11 8	1168 16 0	1050 1 5			
	1118 4 4				28 2 11	Cash at Bank Current Account	18 14 7	
					40 0 0	Do. Deposit Account	100 0 0	118 14 7
	£1118 4 4			£1168 16 0	£1118 4 4			£1168 16 0

STAFF PENSIONS FUND.

377 15 11		To Excess of Assets over Liabilities as per last Balance Sheet ...	401 12 9		—	By Investments (value when acquired):— £289 4s. 4d. 3½% Conversion Stock	226 12 9	
23 16 10		*Add* Excess of Income over Expenditure for year	39 4 10		375 0 0	£371 17s. 1d. War Stock 5% 1929/47 ... (Market Value £611 5s. 7d.)	375 0 0	601 12 9
—		*Add* Transfer from General Purposes Account from accumulation of Funds	200 0 0	640 17 7	26 12 9	,, Cash at Bank		39 4 10
	401 12 9							
	£401 12 9			£640 17 7	£401 12 9			£640 17 7

SPECIAL PUBLICATIONS FUND.

	23 0 0	To Amount prepaid for 1929 ...		18 0 0	1600 0 0	By Investments (value when acquired):— £2115 8s. 10d. 3½% Conversion Stock ... (Market Value £1676 9s. 9d.)		1600 0 0
	3 3 0	,, Sundry Creditors		284 17 1	63 7 0	,, Sundry Debtors		41 10 7
1704 7 3		,, Excess of Assets over Liabilities as per last Balance Sheet	1848 14 7		61 10 7	,, Cash at Bank Current Account	81 17 7	
—		*Less* Excess of Expenditure over Income for the year	278 3 6	1570 11 1	150 0 0	,, Do. Deposit Account	150 0 0	231 17 7
1704 7 3					211 10 7			
144 7 4		*Add* Excess of Income over Expenditure to 31st December, 1927	—					
	1848 14 7							
	£1874 17 7			£1873 8 2	£1874 17 7			£1873 8 2

SPECIAL LECTURES FUND.

To Legacy, Prof. Archibald Liversidge	500 0 0		By Investment (value when acquired):— £1299 9s. 4d. Conversion Stock, 3½% (Market Value £1029 16s. 7d.)		1000 0 0
,, Transfer from General Purposes Account	500 0 0				
,, Excess of Income over Expenditure for the year ...	1 8 2	1001 8 2	,, Cash at Bank		1 8 2
		£1001 8 2			£1001 8 2

... Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be

PRESIDENTIAL ADDRESS.

elivered at the ANNUAL GENERAL MEETING, March 21st, 1929.
By JOCELYN FIELD THORPE, C.B.E., D.Sc., F.R.S.

Co-operation in Science and Industry.

HE past ten years has witnessed a wonderful development of rganised Industry and organised Science in this country, and lthough conditions are still rapidly changing it is nevertheless ossible to look forward and in some measure to determine the osition in which we stand and the prospects for the future. The Var, although one of the greatest economic disasters the world as yet experienced, gave without question a stimulus to discovery nd production which no other event could have occasioned. Especially was this the case in the engineering and chemical inlustries, for the need of new appliances and methods, and the ecessity for producing materials in large quantities and in the hortest possible time, caused the keenest intellects to be brought o bear on the problems at hand, and led to the discovery of new nd important processes many of which have now been introduced nto industry.

It is a principle conceded now even by the enlightened leaders of labour that the universal demand for a higher standard of living necessitates a general increase in the national productive capacity, the term "productive capacity" being used to mean the capacity to render available the potential wealth of the nation in a suitable form. It is chiefly to the chemical and allied industries, mining, metallurgy, etc., that the country turns, because it is their peculiar function, aided by the engineer, to make available its mineral, vegetable, animal and atmospheric wealth. Provided chemical and allied industries are properly organised, they should be in a particularly strong position not only to increase the availability of wealth, but also to guide national policy in questions strongly affecting material prosperity. The age is at hand, if it is not already here, in which the changing majorities of Governments will no longer be able to determine major policies as of war, financial and fiscal, except in directions approved by organised industry. Control by those who hold the keys of national prosperity, that is, of organised industry, is one of the alternatives to class control and is not only a desirable but also an eminently practicable ideal. To achieve it Science and Industry must organise so that they may become strong politically and financially.

Four kinds of co-operation are essential to strength: (1) internal

co-operation, (2) co-operation with pure science, (3) co-operation with Government, (4) co-operation with labour. The last, that is co-operation with labour, is a human question rather than one of science or of policy dependent on science and need not be further discussed, especially since enlightened opinion on the part of employers now realises that labour relations are as vital to prosperity as any other factor.

Internal Co-operation.

Apart from more purely chemical or scientific factors there are two immediate advantages, to be gained by the formation of big combines, in the pooling of capital and the pooling of engineering resources; the establishment of a balance in commodities produced and in the method used for their production being determined mainly by chemical and engineering conditions.

It is evident that very great advantages must attach to the prevention of internal competition in the production of some substance required by more than one member of the combine, as, for example, in the preparation of some common intermediate product required by several manufacturers; but also much is to be gained by the pooling of engineering resources and experience, because many of the new processes which have been devised in recent times depend more upon good engineering for their success than upon any other factor. The chemist calls upon the engineer for workmanship, design and material of the very highest class, and it is precisely in these directions that our engineering science excels. This is particularly true in the case of modern high-pressure processes, none of which was in existence till the end of the war. It is not too much to say that in this branch of chemical engineering Great Britain now leads the world.

The standardisation of methods and the co-ordination of interests as regards production and distribution, the question of price and the prevention of over-production are problems which mainly concern the business organisation of industry, and do not directly affect the relations between Industry and Science. Yet their importance is manifest and in some instances, especially in connexion with the standardisation of methods, the help of the chemist is essential. The need for obtaining a balance in all these factors, a consummation which can only be reached by a pooling of like interests, is obvious.

Probably the best example of the common use of a chemical substance by a number of different manufacturers is that of hydrogen, which is at the present time used in vast quantities for the production of (*a*) methyl alcohol, (*b*) liquid fuels from coal,

(c) ammonia, to mention three of its most recent applications. In pre-war days it was used in large quantities, and still is so used, for the hardening of fat. Nevertheless, the three industrial operations mentioned also represent in a remarkable degree examples of progress and development that have taken place within the last ten years.

Pressure Reactions.—The influence of pressure on reactions was recognised by the organic chemist from the earliest times. The fact that most reactions lead to a diminution in volume gave rise to the obvious suggestion that by the aid of pressure such reactions could be facilitated and possibly in some cases directed. Consequently the organic chemist was accustomed to use autoclaves, sealed tubes and other pressure devices in order to attain the ends he had in view. Later, when the need for catalysts or surface reactants became apparent, the utilisation of pressure in order to further the particular interaction disclosed became essential. The chief difficulties which had to be overcome before such processes could be applied industrially were engineering ones, because it was evident that in order to obtain economical production larger units would be necessary and not only had such units to be made sufficiently strong to withstand the very considerable pressures necessary, but joints had to be made which would remain tight under varying temperatures. That such difficulties have been overcome and that pressure apparatus of very considerable size and capacity are now being used in the chemical industry throughout the world, is an engineering achievement of the very highest order.

Methyl Alcohol and Higher Alcohols.—Organic chemistry, although it covers more compounds than any other section of the science, enjoys this advantage that every one of those compounds can be made, on paper, by using the three commonly occurring substances carbon dioxide, water and ammonia in various proportions. In the early days of the science before the structural theory enabled the organic chemist to produce at will any substance he might require, the sole means of guidance was that derived from a knowledge of the empirical formula indicating the numbers of each atom present in the molecule. Consequently research followed the lines suggested by equations on paper which were based on the same plan as that adopted with inorganic substances. As is well known, the discovery of mauveine by Perkin in 1856 was of this character, and many of Baeyer's earlier researches were of the same nature. Indeed, if one reads Kekulé's "Lehrbuch der Organischen Chemie," which was published at Erlangen in 1861, that is to say, only a few years before the structural theory came into use, the extraordinary difficulties under which research workers in organic chemistry

laboured become apparent. For example, Kekulé gives nineteen formulae for acetic acid which at that time were either in use or had been seriously suggested.

At the present time, although we have the structural theory to help us, we are nevertheless faced with a new unknown quantity, and that is the action and nature of the catalyst by which so many important industrial reactions are brought about. In the earlier days of the science, important and valuable discoveries were made hap-hazard by mixing various substances together and hoping for the best, and even by false reasoning, as, for example, when the photographer, in attempting to fix the colour of methyl-violet by the aid of sodium thiosulphate in the same way as he did the image on his photographic plate, transformed it into a green dye.

At the present time we know nothing of the reasons which determine the action of a catalyst and although we have to hand a vast number of reactions which may be regarded as reasonable and likely to occur should the right conditions be discovered, the search for a catalyst is always attended with difficulty and often ends in disappointment. Prior to the original German patent for the production of methyl alcohol from carbon monoxide and hydrogen, many attempts had been made to realise this very simple reaction even on the laboratory scale. Other reactions readily suggest themselves, such as, for example, the formation of acetic acid from methane and carbon dioxide. As a matter of fact this, and other reactions of a similar type, form the subject of patent specifications, but whether they have been actually realised experimentally must remain an open question in the absence of definite evidence. Our patent system unfortunately lends itself admirably to the production of "blocking" patents, and there is no subject so suitable as organic chemistry as a medium for such patents. The High Pressure Committee of the Department of Scientific and Industrial Research is investigating the nature of catalytic reactions under pressure at Teddington and it is confidently to be expected that Professor G. T. Morgan and his co-workers will be able to help us considerably in our search for the meaning of catalysis as applied to organic reactions, a hope which is justified by the work already published from this laboratory.

The Formation of Liquid Fuels from Coal.—The original process of Bergius, carried out with Westphalian brown coal, has been applied to bituminous coal, but not with the same degree of success. The general method, which consists in "cracking" the coal substances under pressure in the presence of hydrogen, seems over-elaborate to produce a substance of which there is at present too much in the world. Nevertheless a home supply of petrol and fuel

and lubricating oil is highly desirable apart from that produced from Scotch shale oil, which is far too small in quantity to meet a general demand. The solution appears to lie in low-temperature carbonisation, although the economic success of this process seems to depend on the adoption by the public of the coke obtained. This product, which was initially to be called Fuelite but is now to be known as Gloco, is, nevertheless, the Coalite of twenty years ago. Whether it is possible to induce the householder to give up his coal fire is a question that the future alone can answer, but it must be remembered that in town areas where gas is the most valuable product the high-temperature method of carbonisation will still be the more economical financially. It is possible, however, that the liquid products of low-temperature carbonisation which are rich in aromatic phenols will lend themselves to the production of valuable petrols when subjected to vapour-phase "cracking." Indeed, this subject of vapour-phase "cracking" is of the highest importance in connexion with the conversion of higher fractions of the petroleum distillate into petrols, the petrols produced by this method being high in "anti-knock" value. Moreover, the gas formed as a by-product, which is mainly olefinic in character, can be utilised for the formation of numerous alcohols. It is of interest to observe in passing that the reverse process, that is to say, the building up of higher hydrocarbons from those lower in the series, has also received attention and that the production of benzene from ethane, and also from methane by pyrolysis, has been shown by Wheeler and his collaborators to be a practical proposition. The importance of such a conversion to countries like Canada where, daily, millions of cubic feet of natural gas (mainly methane and ethane) are wasted cannot be over-rated.* At the same time the very difficult question of the production of sufficient benzene for the world's needs—a hydrocarbon which has hitherto only been obtainable from coal—is in a fair way to being solved.

The Utilisation of Atmospheric Nitrogen.—The "cosmic scare" raised by Sir William Crookes in his Presidential address to the British Association in 1898 led, indirectly, to the introduction of the arc process for the utilisation of atmospheric nitrogen—a process which is still carried out in Norway.

This was followed by the cyanamide process in 1906 and during the War by the Haber process. From 1913 to well after the

* During 1927, 5,241,000 tons of petroleum were obtained from the Persian oil fields. It is estimated that in the production of this quantity approximately 25,000,000 cubic feet of gas are liberated daily. This gas is mainly methane and ethane, but contains also about 20 per cent. of hydrogen sulphide. At the present time the larger portion of this vast volume of gas is burnt to waste; its utilisation is therefore a problem of urgent moment.

War, the Haber process was the only method of direct synthesis in use commercially, and its rapid development in Germany during the War was the direct outcome of the isolation of that country and the complete absence of the nitrates and nitric acid so essential for the manufacture of explosives and the production of artificial fertilizers. The first plant of this type was established at Oppau in 1913 and operates at a pressure of 200 atmospheres and at a temperature of approximately 500° C. This method is also employed at the Billingham works of Imperial Chemical Industries Ltd., but since the War several new processes have been introduced such as the Claude, the Casale, the Fauser, the Jöst and the Harter processes. These newer methods are in most cases simpler to operate than the original Haber process, and it is now relatively easy to establish a nitrogen fixation process in any country. Moreover, these newer processes enable small synthetic plants to be operated economically and in consequence manufacture can be decentralised. For example, during a recent visit to the United States it was noticed that at the Gibbstown works of the Du Pont company the nitric acid required for the manufacture of the nitro-explosives produced there was being obtained by one of these newer methods. It is evident, therefore, that while the vast quantities of nitrates required for agricultural purposes will continue to be made at the great factories established for that purpose, each industry involving the use of nitric acid for chemical purposes will instal its own plant for its production. In this way the two great uses of nitrogen, that is, as a component of explosives and as a plant food, will become separated and the two types of manufacture will be carried out in different localities. The lesson learnt by Germany during the War is not likely to be lost sight of by other countries, and it can confidently be predicted that every country will ultimately become self-contained as a producer of its own fertilizers and explosives.

Hydrogen.—In all these matters the need for a cheap supply of hydrogen is essential. In the earlier part of the present century the hydrogen required for fat-hardening was produced by the electrolytic decomposition of water. The hydrogen produced in this way is exceptionally pure, but an abundant supply of electricity is necessary, approximately 140 kw.h. per 1000 cu. ft. of gas, that is to say, a quantity that can only be obtained economically in places where abundant electric power is available. Moreover, in this process the oxygen which is also formed cannot be utilised except under special conditions. Modifications of this method are now in operation mainly in the direction of producing the gas from electrolytic cells under high pressure, but although a considerable quantity of hydrogen is still made electrolytically, by far the greater

quantity is now produced by the reduction of steam. The "steam-iron" process, in which red-hot iron is the reducing medium, was the first of these; the Bosch process, which involves the passing of a mixture of steam and water-gas over a catalyst at 400—500° C., followed. It has been estimated that approximately 15% of the hydrogen used is made electrolytically, whereas 70% is made by the water-gas catalytic process. About 12% is made from coke-oven gas by a method which involves the separation of the hydrogen by liquefaction of the impurities present. Coke-oven gas contains approximately 50% of hydrogen and owing to the low calorific value of hydrogen the gas is actually improved in calorific power by its removal. Moreover, during the process of purification considerable quantities of ethylene are isolated—a substance now in demand for the preparation of nitroglycol, a constituent of non-freezing nitro-explosives. It is probable, therefore, that this source of supply will be drawn on more freely in the future and it may even be found economical under special conditions to remove the hydrogen from the gas produced by high-temperature carbonisation in our gas works.

The water-gas catalytic method of producing hydrogen is in use in those places where the original Haber process was installed namely, at Billingham in Great Britain, in the French Governmen Plant at Toulouse, and in the great works of the I. G. Farber Industrie at Oppau and Merseburg. In Germany the extensive deposits of brown coal, which is particularly suitable for use in the Bosch hydrogen process, are available.

The moral underlying the whole of what has been said above i that full industrial prosperity demands still larger chemical com bines and trade associations. The vast chemical organisation whic has been built up in this country under the inspiration and guidanc of Lord Melchett and the great combine known as the I. G. i Germany are indications of the increasing tendency for nations t pool their resources in particular industries and thus stand four-squa to their competitors in the world's markets. By the elimination internal competition, by the pooling of chemical and engineerin resources and knowledge, by the standardisation of methods production on the most economical lines, by the sharing of ra materials, and above all by co-operation with labour the who strength of the nation is focused to a point which enables it to exe the full force of its internal mental and physical power.

Co-operation with Pure Science.

Training.—Chemical trade is at present in the midst of the mo rapid expansion it has ever known and nowhere is the developme

more noticeable than on the research side. This is as it should be, for the researchers are the scouts and it is essential that they should be far ahead of the army (the working process). It is necessary also that the scouts should operate on a broad front in order that no channel of advance should be overlooked merely because it does not lie in the expected direction. The realisation of this principle by the greater manufacturers has led to a strong demand for University-trained men, and the number of research chemists in industry in this country has been estimated at twenty times the number before the War; the demand is still increasing. The Universities have had and are having their work cut out to supply this larger number of adequately trained men, for they have to fulfil the majority if not all of the demands made hy chemical industry. Manufacturers have come to realise that training should be essentially fundamental and that a wide knowledge of the principles of chemical science is a necessity. The vexed question—In what manner is this to be attained?—is heing answered by the gradual adoption of at least a four years' course, although the still more important one—that of the post-graduate course—is not yet settled. In straightforward cases, that is to say, instances involving preparation for those industries which are concerned with the so-called borderland sciences, the issue is clear. For example, the great demand at the present time for chemists with a knowledge of bacteriology, mycology, physiology, and so forth must be met by supplying a post-graduate training in these subjects. Where the hranch of science to be followed lies within the scope of general chemistry, specialisation in that particular branch should form the subject of the fourth-year course. This is undoubtedly the case with that important branch of organic chemistry which deals with the intermediate products from the coal-tar hydrocarbons and the dyes derived from them.

Not only has the far-sighted policy which led the Worshipful Company of Clothworkers to found what is now the Department of Colour Chemistry and Dyeing in this University heen fully justified, but the principles laid down and followed by each successive Head of the Department have served as a model which has been freely followed, both in this country and abroad. The Colour Chemistry and Dyeing Department was, in conjunction with the Textile Industries Department, one of the first buildings to be erected on the present University site. In 1880 these two departments were unique and their subsequent growth has been continuous. For many years the Clothworkers' Company provided their entire maintenance, but on the formation of the University of Leeds in 1904, the rights and management were transferred to

the University. The Company's total monetary contribution towards the provision of this form of University education at Leeds approximates to £250,000, and the most recent extension of these departments, provided by the Clothworkers', was opened in October last.

Each head of the Department (J. J. Hummel, A. G. Green, A. G. Perkin, and F. M. Rowe) has considered it essential that students of colour chemistry and dyeing must be trained primarily as chemists in close co-operation with the pure chemistry, physics, mathematics, engineering, etc., departments, in which a large proportion of the students' time is spent. Merely mechanical, vocational training has never been provided, but the courses have been developed on an increasingly scientific basis in preparation for a career in any branch of industry in which the chemistry of colouring matters, of textile fibres, and of the processes to which they are submitted, plays an important part. Detailed large-scale practice is not taught, although the laboratories are equipped with all types of modern machinery for processing wool, cotton, and artificial silks, the aim being to instil the scientific foundations of such operations. Actually, the training of a student of colour chemistry and dyeing is superimposed upon the normal preliminary training in the pure sciences and is merely a continuation of the latter from the point of view of certain industries. The value and adaptability of this thorough and fundamental scientific and technical training is illustrated by the fact that at the end of his course a student may obtain a position as a chemist in such widely different branches of industry as the manufacture of intermediates and dyes, or of lake pigments, the distillation of tar, the manufacture of artificial silks or other cellulose products, calico printing, or the various specialised branches of bleaching and dyeing, including garment dyeing and cleaning. Although examples of all those industries are to be found in or near Leeds, former students of the Department also occupy important positions in these industries in all parts of this country and abroad. The Department is in close touch with industry and owes much to the interest and generosity of individual firms.

I have thought it desirable to give the above particulars of the Department of Colour Chemistry and Dyeing in the University of Leeds, because they illustrate in a remarkable manner the way in which purely chemical and technical education have been combined to produce men thoroughly trained on both the fundamental and the practical side and who are thus able not only to deal with problems of the moment but also to appreciate and adopt such developments as may occur in the future. It is not the

question of the principle that is involved, because, at the present time, it is fortunately unnecessary to emphasize the truism that mere mechanical or vocational training without fundamental knowledge is useless and cannot meet the needs of rapidly developing industry. It is rather the question of method that is in doubt, and it is therefore important to realise that, so far as the particular industries dealt with are concerned, the Leeds organisation has succeeded in supplying an answer.

A long experience of University teaching has shown me that it is exceedingly difficult to determine whether any particular individual is more fitted to succeed as a process chemist or whether he has that peculiar aptitude which will enable him to carry out effective work in the research laboratory. Unfortunately the positions are not interchangeable. A student who has shown aptitude for research may, if occasion demands, make an excellent process chemist; indeed it often happens that he will have to develop a laboratory method so as to place it, with the help of the engineer, on the unit factory scale. But it is very doubtful if the individual who has shown that he possesses no aptitude for research can be usefully employed in that connexion excepting under control. The only manner in which the presence of the research aptitude can be discovered is bv direct trial and therefore it is always desirable to subject a student to one year's training in research after graduation in order to discover if he possesses this characteristic. After one year's observation it is usually possible to determine whether a man possesses (*a*) originality of thought and method such as will enable him to become a research originator, (*b*) the aptitude for research which will make him a good team worker under direction, (*c*) no aptitude for research of any kind.

Those falling within class (*a*) are rare; those within class (*b*) form the majority. Those falling within class (*c*) are also comparatively rare, because the usual course of training followed in an Honours School is such as to instil a desire for enquiry. But when found, they should be advised to seek one of the minor industrial posts or to secure training in some special branch of technology which will enable them to act effectively as process chemists.

The term "research training" must be interpreted in its widest sense to include training in special branches of chemistry related to the industries as well as more general training in the higher branches of chemical technology. It is evident, therefore, that the field of choice open to a student who has finished his course of fundamental instruction is very large, since it also includes the borderland subjects to which reference has already been made. The choice has to be made by the man himself, guided by such

advice as his teacher can give him. Such guidance will be based on a knowledge of the man's capacity and of the requirements of the moment, but, unfortunately, conditions change so rapidly that the needs apparent at the time the advice is given may be no longer present two years later when the period of training is finished. Nevertheless, the call for men thoroughly trained in the various branches of applied chemistry and in the subjects based on chemistry is likely to increase rather than diminish and it is not correct to say that there is, at the present time, a superfluity of chemists who are unable to obtain employment. There is, naturally, in this branch of science, as indeed in any branch of knowledge, a difficulty in placing second or third class men. The term "third class Honours" ought to be eliminated from our vocabulary, as has been done by at least one of our Universities recently, and it is an open question whether the second class ought not to follow the same path. Nevertheless, one does not make a second class man into a first class one by calling him such, and the need for adjustment evidently belongs to an earlier stage. Men who have shown, during the earlier stages of their studentship, that they are unlikely to obtain anything but a low class in their Degree examination ought to be rigorously excluded from an Honours School. If this were done effectively, we should hear less about the lack of employment for unsuitable men.

Industrial Research in Universities.—At no distant period in the past the great potentiality for research residing in our University laboratories, and in the personnel controlling them, was not available for industrial purposes. The reasons for this were many. For example, industrial research was not regarded as of sufficiently "pure" character to allow of its inclusion in the academic curriculum. There was considered to be something essentially different between "applied" and "pure" chemistry, and this was emphasized in the "eighties" by the formation of the Society of Chemical Industry as a distinct body from our own Society. The Americans knew better than this. They have kept their chemists together as a homogeneous body and the American Chemical Society with its membership of 17,000 represents in no uncertain manner the considered opinion of the whole body of chemists of that country.

The fault lay mainly with our Universities, which were loth to introduce science other than "pure" into their courses of instruction. Hence there arose the multitude of Technical Schools which were originally intended to supply the need for a vocational training without undue reference to the science upon which the training was based. The establishment of new Universities in industrial centres, a period of reform ushered in by the breaking up

of the old Federated Victoria University, soon produced a marked change, and research and instruction in the fundamental principles underlying industrial science gradually passed into the hands most competent to deal with them.

Industrial research both of the fundamental kind and that which arises as the daily outcome of works practice should be and now is carried out for the most part by the firms themselves in their works laboratories. But there are a number of problems, mainly of a "long-sighted" character, which are intimately related to industry. The personnel on the scientific staffs of our Universities are people who have throughout their lives specialised in some particular branch of research, and are therefore eminently fitted to solve problems in their special field. This is now recognised by many leading firms who supply grants to enable post-graduate research workers to investigate specific problems under the guidance of Professors of Chemistry and other directors of research laboratories, and in this connexion must be mentioned the far-sighted policy of Imperial Chemical Industries, Ltd., who give yearly substantial grants to research laboratories in order to enable them to obtain special types of apparatus and appliances which it would otherwise be difficult to procure. Great advances have been made in the country since the War in the development of scientific industry, and every effort must be made to maintain and strengthen the causes which have led to this condition. From the point of view of national prosperity it is essential that active research centres should be maintained and still further developed in our Universities, not only to supply the scientific ability to foster and improve the industries of our own generation, but also to pave the way by discoveries in science for future commercial prosperity.

Team Work.—During the War very valuable work was accomplished by means of team work, by which is meant the solution of some problem by the united efforts of a team of workers under a directing head. There can be no question that this method of attack is usually most effective, especially in a works laboratory where some specific problem may require rapid solution. Its application to the University laboratory is subject to the difficulty that under team conditions the intellectual stimulus which attaches to the individual attack on specific problems is sometimes lacking, and it is in the highest degree desirable that this stimulus should be developed and maintained. Nevertheless, it is always possible so to divide a major problem as to make each section in itself a self-contained research and thus to give each investigator what is essentially a definite subject on which he can work in his own way and according to his own mentality. This, as a matter of fact, is

being done in many research laboratories, and probably one of the best examples is that supplied by the Safety in Mines Research laboratory at Sheffield. Here Professor R. V. Wheeler directs a team of research workers who are engaged on problems connected with the conditions necessary to ensure adequate safety for miners working in coal mines. The problems involved relate to the spontaneous combustion of coal, the use of safety explosive, and the conditions leading to the prevention of the propagation of flame should an ignition of firedamp occur underground. These and many related enquiries are dealt with by a team of research workers employed either at Sheffield or in the new experimental station at Buxton, but each particular problem is assigned to one or two workers and the intellectual stimulus provided by specific investigation is always present.

Frequent meetings and discussions as well as the delivery of lectures by outside workers keep the members of the team in touch with one another and with development generally. There is nothing more destructive of a man's mentality than the feeling that he is merely a cog in a wheel of some machinery of which he has no knowledge; that he is being used as a means of obtaining some substance or result which, as soon as prepared or obtained, passes to someone else for further treatment. Production and sometimes research on these lines is doubtless effective, but it is secured at the expense of individual loss of initiative and craftsmanship. It is the very worst form of instruction that can be imparted in the earlier years of a research worker's training and should be rigorously excluded from our schools of research.

Co-operation with Government.

The Government of this country has already discovered the two most valuable ways in which it can co-operate to the benefit of present and future chemical industry, namely, (*a*) by protecting young and struggling industries against competition from similar but established industries abroad and against competition arising from deflated foreign currency, and (*b*) by promoting research in pure and applied chemistry by financial assistance.

Safeguarding.—The first action under (*a*) was the passing of the Dyestuffs (Import Regulation) Act in December, 1920, an Act which came into operation on January 15th, 1921. It prohibited for a period of ten years the importation into the United Kingdom of all synthetic dyestuffs and all intermediate products used in their manufacture. The position was a peculiar one, because it was obvious that our great textile industries depended on the production of certain types of dyestuffs which had hitherto only been obtainable from

Germany and that several of these dyestuffs could not, at that time, be produced in this country. Definite prohibition was therefore impracticable, and the provision of a tariff would have entailed so high a rate of duty—in order to meet the determined effort which Germany would have made to re-establish its pre-war predominance—that a hardship would have been placed on the consumer. It was generally agreed, therefore, that prohibition tempered by licence was the best solution and the truth of this view is shown by the fact that last year—seven years after the passing of the Act—approximately 10%, about 5,000,000 lb., of the total dyestuffs used in this country were imported under licence, the remaining 90% being produced by home manufacture; an exceedingly satisfactory state of affairs when the position of Great Britain in this connexion before the war is considered. The next application of the safeguarding principle took the form of the Safeguarding of Industries Act, 1921. This Act had two purposes: (1) The safeguarding of a definite list of "key industries" against competition from any source, and (2) provision for the safeguarding of any industry against the effects of the depreciation of the currencies of certain foreign countries.

The schedule of this Act was necessarily couched in very general terms and enacted that an "ad valorem" duty of 33⅓ per cent. could be imposed on certain classes of commodities which experience during the war had shown to be essential for the maintenance and well-being of other industries of national importance.

It was necessary to give the Board of Trade power under the Act to draw up lists embodying the commodities included in the items enumerated in the schedule, and such lists were in due course prepared. The Act also provided that any complaints against the inclusion or omission of any article in the list should be referred to the arbitration of a referee appointed by the Lord Chancellor, whose decision should be final. The schedule of the Act enumerated a variety of commodities, including such general phrases as "synthetic organic compounds" and "fine chemicals," and these were duly interpreted in specific terms in the Board of Trade lists. But it was found extraordinarily difficult to define these phrases in a legal sense. It will be remembered how difficult it was to say whether calcium carbide was an organic or an inorganic chemical, expert opinion by our leading chemists being about equally divided as to the correct answer to the question. In the same way grave difficulties arose as to the correct definition of a fine chemical and the referee found himself faced with a mass of contradictory evidence supplied by persons fully competent to express an opinion. Some twenty cases came before the referee (Mr. Cyril Atkinson,

K.C.) and in every case he supplied a closely reasoned written judgment. The legal interpretation of scientific evidence by scientific experts on scientific matters, especially of definition, is always, however, difficult, and when the desirability of extending the Act beyond the five years provided came up for consideration before a Committee appointed by the President of the Board of Trade, of which Sir William Pope was a member, it was unanimously decided, in a report dated March, 1926, that in place of the Referee alone a tribunal should be set up consisting of the Referee and two scientific referees drawn from a panel appointed by the Lord Chancellor for the purpose. Effect was given to this and other recommendations contained in the Report by the Finance Act of 1926, which continued safeguarding for ten years from August 19th, 1926. Only two cases have so far come up for decision before the newly-constituted tribunal.

The second object of the Act of 1921, namely, the imposition of a *duty of 33⅓ per cent. on "any goods imported from a foreign* country with a depreciated currency if owing to that depreciation such goods were being offered for sale in the United Kingdom at prices below those at which similar goods could profitably be made there and employment in the corresponding industry here was or was likely to be adversely affected," was rendered to some extent abortive, because it was also provided that no order should be made which was at variance with any British treaty or convention with a foreign country. In effect this meant that duties could not be imposed against countries having by treaty or understanding a most-favoured-nation agreement with this country and in consequence duties were only levied against goods of German origin. A wider policy was adopted by the present Government in a White Paper issued in February, 1925, which announced the adoption of a policy by which British industries of substantial importance would be safeguarded if it could be shown that they were suffering from unfair competition owing to (*a*) depreciation of currency operating so as to create an export bounty, (*b*) subsidies, bounties or other artificial advantages, and (*c*) inferior conditions of employment in the competing foreign industries. This policy was given effect to by the Finance Acts of 1925, 1926, 1927 and 1928, by which duties were imposed in a number of cases on articles falling within the above categories.

Agricultural Research.—Of all the industries which are and have been served by chemistry, agriculture stands in a special position in so far as the Government have placed at its disposal an organised and free advisory service. There are at present 21 Advisory Chemists in England and Wales, each having his headquarters a

some appropriate educational centre. Every bona-fide farmer is entitled to their advice (which normally involves a visit to the farm) without being involved in any expense whatever. Farmers are availing themselves of this service more and more every year and the industry is consequently in a far more favourable position than it was twenty years ago.

There is a great deal of valuable reciprocity here. The Advisory Chemist is expected to carry out fundamental scientific investigations that relate or appear to relate to the farming problems he meets. This work has enlarged our knowledge of the constitution of the soil, which new knowledge has in turn enhanced the utilitarian functions of the Advisory Chemist.

For generations farmers in many areas have suffered a complete failure of their barley crop. In more recent years, sugar beet—for no reason apparent to the farmer—has similarly and unexpectedly failed. It is not too much to say that the work of the Advisory Agricultural Chemists has now made it possible for a farmer to know almost with certainty before he arranges his cropping where those crops are likely to fail and to be informed of the only measures which will ensure their success.

No less in animal husbandry than in crop husbandry are the services of the chemist of great economic value to the farmer. It is no unusual thing for the Advisory Chemist to adjust uneconomical and ill-balanced rations to stock in a way which has saved the farmer a deal of money. The cost of producing milk has been reduced by as much as 4*d.* a gallon and the economy effected in feeding fairly large herds is sometimes between £40 and £50 a month.

The Promotion of Research.—The scheme for the organisation and development of scientific and industrial research was given in Mr. Arthur Henderson's memorandum of 23rd July, 1915, which was issued as a White Paper (Cd. 8005). The Advisory Council was constituted by an Order in Council of the 28th July, 1915, the terms of reference being " to recommend proposals (i) for instituting specific researches; (ii) for establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades; and (iii) for the establishment and award of Research Studentships and Fellowships."

The Order also stated that " The said Council may itself initiate such proposals and may advise the Committee (*i.e.*, the Committee of Council for the organisation and development of scientific and industrial research, constituted by the same Order) on such matters whether general or particular relating to the advancement of trade and industry by means of scientific research."

The 13th Annual Report of the Department has recently been issued and shows that development along all the lines indicated in the terms of reference has been initiated, and that great progress has been made in giving effect to the intention of the scheme.

Specific Researches.—Apart from the work which is being carried out by the special research stations founded by the Department, notably the Fuel Research Station, the Forest Products Research Station, the Chemical Research Laboratory, Teddington, and the Low Temperature Research Station of the Food Investigation Board, many other specific researches are in progress at various research institutions throughout the country. At the same time the Department supports specific researches of a fundamental kind which are of wide interest both from the scientific and the practical point of view and the furtherance of which is likely to lead to results of national importance. Examples of these may be given in the work on *X*-rays, which is now entering a stage which shows not only that the information procurable by this method of analysis is certain to give us knowledge of intimate molecular structure, but that it is also applicable to such important practical uses as the determination of the structure and properties of alloys. Assistance is also given to the work which is being carried out by Professor Bone at the Imperial College on gaseous reactions at high pressures, and this laboratory, which has also received substantial financial assistance from Imperial Chemical Industries, Ltd., is now adequately equipped to prosecute research in this most important field.

Research Associations.—The policy instituted by the Department, by which Research Associations in various industries were founded on the basis of annual grants equivalent to the annual subscriptions o members of the Associations, has led to the formation of twenty-four of these bodies. At the outset it was considered that a period of five years was sufficient to give this experiment in co-operative research a fair trial and that at the end of this period State assistance could cease. Experience showed, however, that except in certain special cases five years was not long enough to enable an Association to prove its value by the results of the work accomplished, and an extension of State aid was granted for a further period of five years. The report of the Department for 1927—28 shows that a memorial was received from nineteen Research Associations praying for a continuance of financial assistance on the same basis for a further period of ten years. There can be no question that the experiment has proved a success and that the value of co-operative research in industry has been established. The Department has, therefore, rendered a valuable service to the industrial community and its initial policy has been fully justified. Nevertheless the

time has arrived when the varying appeal which the necessity for scientific investigation makes to different industries has made itself manifest and the Department feels that any further support on general lines would no longer be justified. It proposes, therefore, to treat each case on its merits.

Research Studentships and Fellowships.—The third term of reference, namely, "for the establishment and award of Research Studentships and Fellowships," was rendered necessary in order that properly trained personnel should be available to meet the requirements of rapidly growing industry and also that the Research Associations which were about to be set up should be adequately staffed by men thoroughly trained in the methods of research.

Prior to the war research training was imparted only to a comparatively few students who had passed high in their final examinations and had thus obtained one or other of the post-graduate scholarships or fellowships provided by most Universities. Schools of research were small, because those whose parents could not afford to pay for a five years' course had to seek employment as soon as they had taken their Honours Degree. The provision of Students' Maintenance Allowances by the Department has, therefore, enabled many men who would otherwise have had to pass into industry at the end of the three years' course to stay at the University for one or two years longer and in this way many students, fitted by temperament to make useful research workers, have been prevented from taking too early employment. This policy is undoubtedly in the national interests, because it provides for a steady stream of research workers which could not otherwise be produced. That the policy has been justified is shown by the figures given for the year 1926—27, when out of 165 students provided with maintenance grants 59 only sought renewal, the remaining 106 being either absorbed into industry or into posts of other kinds. The call for adequately trained research workers in science and especially in chemistry is increasing. Every head of a research school knows that he can always place a thoroughly trained man and he is frequently in the position of having no men available when application is made to him for research workers. It is therefore very disquieting to realise that the policy of the Department in connexion with the provision of maintenance grants for students in training appears to be changing, for whereas the number of such grants (including research workers and assistants) was 275 in 1925—26, it has fallen to 186 in 1927—28. The outlook is serious, because it is quite impossible for the Universities to provide funds for post-graduate training in any way commensurate with the present-day requirements of industry, and as the average science student is usually drawn from a

comparatively poor class it is not likely that the necessary money for an extended course will always be obtainable from parental sources. No doubt in the future the Universities will be able to acquire adequate funds for this purpose from benefactors who appreciate the need, but that time is not yet come and meanwhile it is essential that the State should provide the means for helping to meet this very real national difficulty.

Every director of a research school has had to tell some promising student who wishes to undergo post-graduate training and who is, without question, likely to profit by such training, that no funds are available to enable him to extend his course and that he must, therefore, seek any minor post that may be open to him. The loss of such a man is a national loss, because his training is broken off at the stage where even one extra year would have enabled him to become a useful member of a research organization, whereas, in the circumstances, he has to take up some position, probably one involving merely routine work, where the value of his early training will be lost and his initiative and enthusiasm destroyed. It is, therefore, to be hoped that the diminution in the number of research grants is merely a temporary expedient and that it does not indicate a reversal of a policy which has proved so fruitful during the past twelve years and has shown itself to be an essential part of research development in this country.

CXII.—*The Polarity of the Halogens in Solutions of Pyridinium and Allied Dichloroiodides.*

By THOMAS HAROLD READE.

THE reactions of pyridinium dichloroiodide, phenyltrimethylammonium dichloroiodide, and tetramethylammonium dichloroiodide have been investigated. The substances show very close similarity with rubidium dichloroiodide, which was studied by Sullivan (*Z. physikal. Chem.*, 1899, **28**, 539), for the dissolution of each in water was accompanied by separation of the chlorine and iodine atoms, the former as chloride ion and the latter as hypoiodous acid—chlorine gas and iodide ion being absent. A satisfactory reaction formula must express these facts. Since hypoiodous acid can give iodine, or iodide, only by reduction, *e.g.*, at a cathode, whereas iodide gives iodine only by oxidation, *e.g.*, at an anode, it is convenient to assign a positive charge to iodine in the former condition. The electrical conductivity of liquid iodine chloride and iodine bromide and of solutions of iodine in several solvents is another indication of the existence of positively charged iodine atoms. In the presence of water, doubtless, these discharge themselves by combination with negatively charged hydroxyl ions, forming hypoiodous acid. The following equation satisfactorily expresses the results obtained in this investigation:

$$\overset{+}{B}\overset{-}{Cl}\overset{+}{I}\overset{-}{Cl} + H_2O \longrightarrow \overset{+}{B} + \overset{-}{Cl} + \overset{+}{H} + \overset{-}{Cl} + IOH.$$

The formula is intended to denote that the oppositely charged halogen atoms and the radical B are held together by electrostatic forces, like the sodium and chlorine atoms in sodium chloride, but it does not define the degree of electrolytic dissociation which the compound undergoes when dissolved. In water, this is certainly large; in dilute hydrochloric acid, less; and for a 0·001*M*-pyridinium dichloroiodide solution in *N*-hydrochloric acid, the dissociation is still appreciable. The effect of changes in hydrion and chlorine-ion concentration on the degree of dissociation of dichloroiodides has been measured.

EXPERIMENTAL.

Organic dichloroiodides give brown solutions in water, light brown solutions in *N*-sodium chloride, and bright yellow solutions in hydrochloric acid. These will be considered separately.

Procedure.—In a darkened laboratory, 0·001*M*-solutions of the dichloroiodides were made up below 50° with water free from carbon dioxide in steamed flasks of Jena glass. Measured portions at 15° were mixed with a solution of Lintner's soluble starch and the

appropriate reagent in steamed test-tubes which were then corked, and kept under observation.

1. *Effect of Water.*—The deep brown 0·001*M*-solutions, which had an odour like that of iodine, remained brown in the presence of starch for more than 5 hours and then became blue. More dilute solutions (0·001—0·00005*M*) became blue more rapidly.

TABLE I.

*Time of appearance of blue colour throughout the solution.**

Conc. (molar).	Pyridinium dichloroiodide.	Phenyltrimethylammonium dichloroiodide.
0·001	*after* 5¼ hours	*after* 5¼ hours
0·0006	2¾ ,,	*after* 5¼ ,,
0·0004	76 minutes	3 ,,
0·0003	3 ,,	40 minutes
0·00025	less than 2 ,,	5 ,,
0·00020, 0·00015, 0·00010	,, ,, 1 minute	less than 1 minute
0·00005	colourless	colourless (discarded after 3 hours)

* When the starch solution was floated on to the dichloroiodide solution the first appearance of blue colour was as a ring at the surface of contact o glass, starch solution, and dichloroiodide solution; this disappeared on shaking. The times given in Table I refer to the appearance of blue colour throughout the whole of the solutions, which had been mixed by shaking a the beginning of the time period.

2. *Electrolysis.*—When the 0·001*M*-aqueous solution was submitted to electrolysis between platinum wire electrodes in the presence of starch, a blue colour appeared around the cathode in 5 minutes (*E.M.F.*, 2 volts; 35 ⟶ 20 micro-amps.). The anode solution remained light brown. The experiment was repeated many times with the same result. The blue colour did not appear until the circuit was completed. Reversing the direction of the current with the electrodes *in situ* caused the blue colour to appear around the new cathode and dissipation of that around the old cathode. Hydrogen escaped from the cathode. In one experiment lasting 18 hours, a few tiny yellow crystals, which were probably the tetrachloroiodide, were deposited on the anode.

The production of the blue colour at the reducing pole is a fact of theoretical significance, since a substance acquires an electron when it is reduced. Even more significant, however, is the absence of the blue colour at the oxidising pole, showing that iodide ions are absent.

3. *Acidity of the Aqueous Solutions.*—The 0·001*M*-aqueous solutions were decidedly acid to litmus; they dissolved magnesium wire with evolution of hydrogen, and production of a blue colour i

arch was present. Although this result might be attributed to ssociation of the pyridinium complex, a similar reason cannot be ıt forward to explain the acidity of tetramethylammonium or ıenyltrimethylammonium dichloroiodide. The natural inference that dichloroiodides as they enter into solution withdraw hydroxyl ns from water, leaving the solution acid.

4. *Action of Carbon Disulphide.*—Almost the whole of the iodine as removed from a 0·001*M*-dichloroiodide solution in water by peated shaking with carbon disulphide, the aqueous layer entually becoming colourless. It remained colourless also after c addition of starch, but became blue on addition of potassium dide and starch, possibly owing to the presence of iodate.

5. *Action of Sodium Hydroxide.*—The addition of sodium hydroxide ee from iodide) to the 0·001*M*-dichloroiodide solution in presence starch caused the appearance of a blue colour at the times stated Table II, from which it is seen that, whereas high concentrations alkali prevent formation of the blue colour, intermediate concentrations cause its instantaneous formation, namely, when the olecular ratio of dichloroiodide to sodium hydroxide is 1 : 1 or 2.

TABLE II.

Action of sodium hydroxide on phenyltrimethylammonium dichloroiodide in presence of starch solution.

Total vol., 10 c.c. Vol. of 0·001*M*-$C_6H_5 \cdot NMe_3ICl_2$, 5 c.c.

ol. of NaOH.	Appearance of blue.	Vol. of NaOH.	Appearance of blue.
	not within 2¼ hours	1·2 c.c. of 0·01*N*	at once
.c. of 0·001*N*	2¼ hours	1·4 ,, ,, ,,	10 mins.
,, ,, ,,	½ hour	1·6 ,, ,, ,,	
,, ,, ,,	2 mins.	1·8 ,, ,, ,,	permanently
,, ,, ,,	at once	and larger amounts	colourless

Pyridinium dichloroiodide behaved similarly.

The non-production of the blue colour by an excess of sodium droxide is attributed to conversion of iodine into iodide, hypolite, and iodate. The accelerated production of the blue colour at e lower concentrations is attributed to upset of the balance of versible reactions due to removal of hydrogen ions. These are ssibly the following :

$BClICl + H_2O \rightleftharpoons B^{\cdot} + H^{\cdot} + 2Cl' + IOH \rightleftharpoons B^{\cdot} + H^{\cdot} + 2Cl' +$
$[IO_3 + \frac{2}{5}I_2 + \frac{2}{5}H_2O.$

$I_2 + 2NaOH \longrightarrow NaI + NaOI + H_2O.$

$NaI + I_2 +$ starch $\longrightarrow$ blue substance.

6. *Action of Sodium Chloride.*—High concentrations of sodium oride (free from iodide) accelerate the production of the blue our with starch and a dichloroiodide, as shown below.

TABLE III.

Action of sodium chloride on dichloroiodide in presence of starc
(Total vol., 10 c.c.)

Pyridinium dichloroiodide (6 c.c. of 0·001*M*).		Phenyltrimethylammonium dichloroiodide (5 c.c. of 0·001*M*).	
NaCl.	Blue appears in	NaCl.	Blue appears
0	177 mins.	1 c.c. of 0·1*N*	135 mins.
1 c.c. of 0·01*N*	142 ,,	5 ,, ,, 0·1*N*	5 ,,
1·5 ,, ,, 0·1*N*	20 ,,	1 ,, ,, *N*	immediately
4 ,, ,, *N*	immediately		

7. *Action of Hydrochloric Acid.*—*A transient blue colour w obtained by dropping 4N-hydrochloric acid into 0·001M-dichlo* iodide solution containing starch. The blue colour changed to pi in a few seconds and soon became almost colourless, faintly yello No blue colour was obtained if the dichloroiodide solution was mc dilute than 0·001*M*.

Sulphuric acid produced no visible change in dichloroiodi solutions containing starch; sulphuric acid and sodium chlori together behaved like hydrochloric acid.

8. *Action of Iodides.*—An intense blue colour was obtained adding potassium iodide to aqueous dichloroiodide solutions co taining starch, iodine sometimes separating as a solid.

9. *Reducing Agents.*—In the absence of iodide, the gradu addition of 0·01*M*-sodium thiosulphate to 10 c.c. of 0·001*M*-dichloi iodide solution in water in presence of starch gave a deep blue colo which was discharged by heating or by excess of thiosulpha Sulphurous acid, sodium sulphite, stannous chloride, and mo slowly, ferrous sulphate, zinc dust, and magnesium gave the sar characteristic reaction.

The amount of thiosulphate needed to produce the blue colour a just to discharge it (in the absence of iodide) varied according to t speed of titration from 0·86 to 0·49 of the amount needed wh potassium iodide and acid were present in excess.

10. *Oxidising Agents.*—Iodic acid, ferric chloride, cupric sulpha and ammonium persulphate gave no visible sign of reaction wi dichloroiodides and starch, but perhydrol and nitrous acid, whi are occasionally used as reducing agents, gave the blue colo immediately.

The interpretation placed on these experiments may be th summarised: Aqueous solutions of dichloroiodides undergo a chan of composition with time. At first, they are strongly acid, are ri in chlorine ions, yield iodine to carbon disulphide with formation

ıt do so at once if neutralised or made slightly alkaline, or if iodide added, or in the presence of a large excess of sodium chloride, give ıe blue colour during electrolysis at the cathode only, and give it ı treatment with inorganic reducing agents but not with oxidising ;ents (except perhydrol and nitrous acid). These solutions, .erefore, contain iodine but no iodide; they contain some oxidising ;ent capable of removing iodide ions faster than they are produced ; the action of iodine on the glass (during the first few hours); the :idising agent is easily destroyed by reduction and it undergoes ɔw spontaneous decomposition: it is probably hypoiodous acid, hich is known to change into iodine, iodic acid and water; or ɜrhaps the compound I_3OH.

11. Cofman (J., 1919, **115**, 1044) has shown that hypoiodous acid teracts rapidly with phenols with production of iodophenols and ıter, and can be estimated in this way. If, therefore, the conusions drawn from experiments 1 to 10 are correct, the addition of ırious phenolic substances to an aqueous solution of a dichlorodide containing starch should produce a blue colour owing to the ɾmation of iodide by the action of molecular iodine, I_2, on the glass. he following substances produced this effect: phenol, salicylic :id, α- and β-naphthol, cuminol, eugenol, euthymol, *o*- and *p*-cresol, hydroxybenzoic acid, *m*-hydroxytoluic acid, gallic acid, tannic :id, salicylaldehyde, and guaiacol; whereas a blue colour was not :veloped with benzoic acid, picric acid, anthraquinone, chloranil, ıenanthraquinone, α- or β-naphthaquinone, thymoquinone, anisole, ıisic acid, or phenetole. The presence of hypoiodous acid in ɿueous dichloroiodide solutions was thus confirmed, and the reason hy these solutions did not at first give a blue colour with starch, ⁄en though they contained iodine, either free or very loosely ɔmbined, became clear.

12. *Action of Amines.*—Since aromatic amines and phenols have ıany chemical properties in common, trial was made to ascertain if ıe former also would remove the hypoiodous acid, and allow the ›lution to develop the blue colour with starch. This took place nmediately when dichloroiodides in aqueous solution were treated ith aniline, *o*- or *p*-toluidine, *o*-4-xylidine, *o*-anisidine, α- or naphthylamine, sulphanilic acid, diethylaniline, phenylhydrazine, : morphine sulphate, and more slowly with acetanilide, *o*-, *m*-, · *p*-nitroaniline, 2-nitro-*p*-toluidine, phenyl-α-naphthylamine, or henyl-β-naphthylamine.

13. *Action of Unsaturated Compounds.*—The following unsaturated ›mpounds gave the blue colour under conditions similar to those ›corded in section 12: cinnamic acid, cinnamaldehyde, terebene, nylene, and alcoholic stilbene. Ethyl or benzyl alcohol, acet-

aldehyde, benzaldehyde, dibenzoylstyrene, urea, alcoholic ethylamine, benzil, benzoin, and hydrobenzoin were without action.

14. *Pyridinium and* p-*Bromophenyltrimethylammonium Dichloroiodides in Hydrochloric Acid.*—These yellow solids are recrystallisable from concentrated hydrochloric acid. They are sparingly soluble in N-hydrochloric acid, giving about 0·001M-solutions the colour of which is like that of the crystals. The solutions do not give a blue colour with starch alone, but give successively red, purple, and blue colorations and then become colourless on gradual addition of sodium thiosulphate, sulphurous acid, nitrous acid, or ferrous sulphate, but not on addition of ferric chloride, potassium iodate, ethyl alcohol, or acetaldehyde.

15. *Electrolysis.*—Electrolysis of the dichloroiodides in $2N$-hydrochloric acid between platinum electrodes in presence of starch gave at the cathode a similar set of colour changes from red through purple to blue in the course of 6 hours, 25 microamps. being used; the anode solution remained yellow and deposited yellow crystals of the tetrachloroiodide on the anode.

16. *Perhydrol.*—This decolorised dichloroiodides in N-hydrochloric acid with evolution of oxygen. In presence of starch, a blue colour appeared only after 5 hours, and disappeared after 18 hours. The greater the amount of hydrochloric acid, the slower the production of the blue colour. The colourless solution finally obtained gave (*a*) with thiosulphate a blue colour, discharged by dilute hydrochloric acid or by an excess of thiosulphate, (*b*) a large precipitate of iodine after addition of potassium iodide, and (*c*) a colourless solution when treated with iodic acid, and hence contained iodate but not iodide.

17. *Halides.*—With potassium iodide, hydrochloric acid solutions of dichloroiodides gave an instant deep blue colour in presence of starch. With potassium bromide, a deeper yellow colour but no blue was obtained; addition of sodium thiosulphate to this solution gave successively a deep red, a blue, and a colourless solution.

18. *Immiscible Solvents.*—Carbon disulphide or benzene became pink, and ether became yellow, when shaken with dichloroiodides in hydrochloric acid. After separation and washing with water, the organic liquid failed to give a blue colour with starch solution unless thiosulphate or iodide was added.

19. *Action of Phenols.*—No blue colour was obtained in presence of starch on addition of phenols to the dichloroiodides in N-hydrochloric acid. Interaction between the phenol and the solution nevertheless took place, and was studied quantitatively (see section 25).

The hydrochloric acid solutions exhibit greater similarity of reaction with aqueous solutions than was expected from their

different appearances; but they react more slowly, and they contain less hypoiodous acid and very little (if any) free iodine.

20. 0·001*M*-*Dichloroiodide Solutions in Aqueous Sodium Chloride.*—The colour of the dichloroiodides in aqueous sodium chloride varied from a light brownish-yellow with 0·1*M*- to a deep brown with 0·001*M*-sodium chloride, the solutions having the odour of iodine. Unlike the behaviour in water or in hydrochloric acid, solutions in aqueous sodium chloride of 0·001, 0·004, and 0·020*M*-concentration gave a blue colour with starch in 5 minutes. The solution in 0·1*M*-sodium chloride remained light brown, but became blue on dilution, a 1 in 2½ solution taking 72 hours, and a 1 in 5 solution, 2½ hours; more dilute solutions failed to turn blue.

21. *Action of Sodium Hydroxide on Dichloroiodides in Aqueous Sodium Chloride.*—Sodium hydroxide had a greater effect than water in accelerating the production of the blue colour with starch, the greatest effect being obtained when the ratio sodium hydroxide : dichloroiodide was about 2 : 1; the blue colour then appeared within 2 minutes. No blue colour appeared when the ratio was 4 : 1. The blue colour faded after a few days when the solutions were exposed to the action of light (in June) through a window facing west. The inner surface of the corks of the test-tubes became slightly yellow. At the end of the experiment shown in Table IV, iodide and hypoiodite were absent, and iodate was present in amount roughly proportional to the original dichloroiodide.

TABLE IV.

Action of sodium hydroxide (1 c.c. of 0·001*N*-solution) on 0·001*M*-pyridinium dichloroiodide in 0·1*M*-sodium chloride solution.

		Blue colour with starch.				Blue colour with starch.	
Solution (c.c.).	Water (c.c.).	First appearance.	Last appearance.	Solution (c.c.).	Water (c.c.).	First appearance.	Last appearance.
1	9	5 mins.	4 days	6	4	24 hours	21 days
2	8	17 hours	7 ,,	7	3	2 days	14 ,,
3	7	17 hours	9 ,,	8	2	4 ,,	14 ,,
4	6	22 ,,	12 ,,	9	1	5 ,,	12 ,,
5	5	24 ,,	28 ,,	10	0	9 ,,	12 ,,

It is seen from the last column that the blue colour disappeared most slowly when the molecular ratio of sodium hydroxide : dichloroiodide was 1 : 5, which is clearly insufficient to neutralise the total acidity demanded by the equation $BClICl + H_2O \longrightarrow BCl + HCl + IOH$ but would suffice to remove the iodic acid formed in accordance with the further equation $5IOH \longrightarrow HIO_3 + 2H_2O + 2I_2$. No reason for this behaviour is yet known, but the large concentration of sodium chloride is a factor to be considered.

22. *Electrolysis of Dichloroiodides in Sodium Chloride Solution.*—The electrolysis of 0·001*M*-pyridinium dichloroiodide in 0·1*M*-sodium chloride solution containing starch in a U-tube with platinum wires as electrodes (2-volt battery) gave a blue colour around the cathode in 2 minutes; the anode solution remained light brown. Reversal of the current with the electrodes *in situ* produced a blue colour around the new cathode within 2 minutes.

23. *Acid.*—The blue colour with starch given by dichloroiodides in *dilute* sodium chloride solution was discharged by dilute sulphuric acid (but was *not* due to hydrolysis of the starch). This loss of colour was more marked the greater the concentration of either the acid or the sodium chloride. From colorimetric trials, small changes in the acidity had the same effect as large changes in the sodium chloride concentration. In Table V the intensity of the blue colour decreases from left to right.

TABLE V.

Intensity of the blue colour produced with starch, pyridinium dichloroiodide, sodium chloride, and dilute sulphuric acid.

(Total vol., 11 c.c.)

	Proportions in g.-mols.												
Pyridinium dichloroiodide $\times 10^{-6}$	1	1	1	1	1	1	1	1	1	1	1	1	1
Sodium chloride $\times 10^{-6}$	1	1	4	1	1	4	4	20	4	20	20	20	4
Sulphuric acid $\times 0{\cdot}5 \times 10^{-4}$	6	7	6	8	9	7	8	6	9	7	8	9	10
Colour	Blue				Light-blue				Less blue			Colourless	

The colours were compared 20 minutes and 20 hours after the beginning of the experiment, and the same order was recorded in each case, though there was a general slight loss of blueness observed at the longer time.

24. Although convincing reasons for certain idiosyncrasies recorded in this section cannot yet be given, in their general characteristics *the sodium chloride solutions of dichloroiodides lie* between aqueous solutions and hydrochloric acid solutions. It seems likely that hydrochloric acid solutions and concentrated sodium chloride solutions give no blue colour with starch because formation of free iodine is prevented by the high chlorine-ion concentration. However, with less sodium chloride, free iodine due to the change $5IOH \longrightarrow HIO_3 + 2H_2O + 2I_2$ is probably present; and since Skrabal (*Monatsh.*, 1911, **32**, 167) has shown that electrolytes accelerate this change, these solutions are probably sufficiently rich in iodate and iodine to allow the latter to form sufficient iodide to give the blue colour with starch (by attacking the glass); for it is probable that in nearly neutral solution iodic acid decomposes iodides more slowly than does hypoiodous acid.

Freshly prepared aqueous solutions of dichloroiodides probably contain more hypoiodous acid than free iodine, and so they destroy iodide formed from the glass quickly enough to prevent the blue starch–iodide–iodine complex from being formed.

25. *The Influence of Hydrogen Ions and Chlorine Ions on the Composition of Solutions of Dichloroiodides.*—The rate at which phenol interacts with dichloroiodides was measured in mixtures of aqueous sodium chloride, sulphuric acid, and hydrochloric acid, in various proportions, so as to compare the relative retarding effects of the hydrogen and chlorine ions on the dissociation of the dichloroiodide, as computed from the content of hypoiodous acid. For the latter can be estimated by the difference in thiosulphate titre of aliquot portions containing potassium iodide, before and after the addition of phenol, which in acid solution removes hypoiodous acid quantitatively but does not act directly on iodine chloride (Cofman, *loc. cit.*).

Procedure. 0·001*M*-Solutions of pyridinium or phenyltrimethylammonium dichloroiodide were made up below 30° in the acid–sodium chloride solutions of the requisite composition and were then cooled rapidly to 2°, the volume being 848 c.c. 48·7 C.c. were withdrawn for computation of the concentration at time 0, by addition to potassium iodide and titration of the liberated iodine by 0·002*M*-sodium thiosulphate (x). Into the remainder, at time 0, 48·7 c.c. of 5% phenol solution at 2° were blown, and mixed by shaking for 40 seconds. Measured portions were then withdrawn rapidly by pipettes, discharged at recorded times into potassium iodide solution, and titrated with 0·002*M*-thiosulphate solution with starch as indicator. The phenol being in large excess, nearly constant values were obtained for the velocity coefficient by use of the formula $k = 2{\cdot}3\ (\log_{10}C_1 - \log_{10}C_2)/(t_2 - t_1)$, t being recorded in seconds and C in c.c. of 0·002*M*-thiosulphate. These results are summarised in Table VI, in which $\bar{k}$ is the arithmetic mean of the individual values of k when the difference $C_1 - C_2$ exceeded 1·5 c.c. of thiosulphate for 25 c.c. of dichloroiodide solution—other values being excluded. Column 5 shows the statistically calculated probable error of $\bar{k}$, and is of the order of 1 to 2% owing to end-point difficulties with the very dilute thiosulphate in acid solution. Column 6 shows roughly the order of the initial concentration of hypoiodous acid expressed as a percentage of the total titratable halogen, as computed from the mean $\bar{k}$ and less accurate C_1 and x.

From Table VI, it is evident that chlorine ions have decidedly the greater retarding effect, and hence it is probable that there is a stage intermediate between the undissociated dichloroiodide and its final ionised and hydrolysed products, such that the first and second

TABLE VI.

$0{\cdot}001M$-Pyridinium dichloroiodide.

Added electrolytes. M-NaCl.	N-HCl.	N-H_2SO_4.	k.	Probable error of k ($\pm$).	Initial IOH%.
—	1·0	—	0·0603	0·0007	1·8
0·5	*0·5*	—	*0·1032*	*0·0013*	*2·6*
0·75	0·25	—	0·1567	0·0019	3·4
0·90	0·10	—	0·3705	0·0018	3·8
0·99	0·01	—	2·417	unknown	22
—	0·5	0·5	0·2808	0·0046	7
—	0·4	0·6	0·432	0·0055	(2)
—	0·3	0·7	0·662	0·0092	10

$0{\cdot}001M$-Phenyltrimethylammonium dichloroiodide.

—	1·0	—	0·0672	0·0017	2
0·5	*0·5*	—	*0·0965*	*0·0019*	*1*
0·75	0·25	—	0·202	0·0024	3·7
0·9	0·1	—	0·389	0·0049	4·5
—	0·5	0·5	0·308	0·0037	5
—	0·4	0·6	0·456	0·0055	6·5
—	0·3	0·7	0·849	0·0090	13

changes are retarded by hydrogen and chlorine ions to different extents: Undissociated BCIICl + water $\rightleftharpoons$ Intermediate state $\rightleftharpoons$ B˙ + Cl′ + IOH + H˙ + Cl′. The most likely alternatives for this intermediate state seem to be (*a*) B˙ + Cl′ + ICl + (water), (*b*) B˙ + Cl′ + I˙ + Cl′, (*c*) BClIOH + H˙ + Cl′, (*d*) B˙ + [ClIOH]′ + H˙ + Cl′. Of these, the substance BClIOH and its ion [ClIOH]′ are hypothetical and have never been isolated, nor their existence inferred from other properties; nevertheless they might exist temporarily. If, however, the supposition of their existence is considered unlikely, the choice of a suitable intermediate state lies between (*a*) and its ionised form (*b*). It is difficult to believe that iodine monochloride in (*a*) could be wholly un-ionised, for it is well known to be an electrolyte when prepared in more usual ways. The most probable *intermediate state seems therefore to be* (*b*) *or* a mixture of (*b*) and (*a*), either of which involves recognition of a positively electrified iodine atom having a separate existence, though momentary in the presence of water, owing to its affinity for the hydroxyl ion with which it forms hypoiodous acid, or "iodine hydroxide" as others have named it.

Thus in the reactions

$$\text{BClICl} \underset{\text{change 1}}{\rightleftharpoons} \text{B}^{\cdot} + \text{Cl}' + \text{I}^{\cdot} + \text{Cl}' \underset{\text{change 2}}{\overset{+\text{ water}}{\rightleftharpoons}} \text{B}^{\cdot} + \text{Cl}' + \text{IOH} + \text{H}^{\cdot} + \text{Cl}'$$

chlorine ions govern the extent of change 1 without influencing change 2, whereas hydrogen ions affect change 2 but not change 1, the tendency for the transformation from left to right being retarded by the presence of substances with these common ions. If this inter-

pretation of these experiments is valid, the first change is the very simple one of the electrolytic dissociation of a double salt,* as opposed to the hydrolysis of a complex salt, and has constitutional significance. The device of writing + and — signs above the atoms in dichloroiodides, as was previously suggested for quaternary ammonium trihalides in general (J., 1926, 2528) to acconnt for irregularities in halogen replacement experiments, derives support from the experiments now recorded, and seems to be more than a mere mnemonic. The existence of charged atoms, however, does not prevent the substance from being in solution but undissociated, when the concentrations of chlorine ions and hydrogen ions are high owing to deliberate addition of substances containing these ions.

Summary.

Pyridinium and phenyltrimethylammonium dichloroiodides are highly dissociated in water, the solutions being rich in hydrogen ions, chlorine ions, hypoiodous acid and its decomposition products; molecular chlorine and iodide ions are absent. The retarding effect of electrolytes containing chlorine ions and hydrogen ions on the dissociation of the dichloroiodides has been measured. The probability that dichloroiodides are double salts containing a highly reactive, positively charged iodine atom is discussed. Hypoiodous acid behaves similarly towards phenolic substances and aromatic amines.

MARISCHAL COLLEGE,
UNIVERSITY OF ABERDEEN. [*Received, February 15th*, 1929.]

CXIII.—*Methoxy-derivatives of Thioxanthone.*

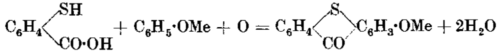
By KENNETH CHARLES ROBERTS and SAMUEL SMILES.

DURING the reduction of 1 : 4-dimethoxythioxanthone it was observed that the substance was soluble in concentrated hydrochloric acid and that the red hydrochloride formed yielded a ferrichloride and a chloroplatinate. Other methoxy-derivatives of thioxanthone then at hand did not exhibit this behaviour; hence the experiments now described were made with the purpose of determining the character of these salts and the structural conditions necessary to their formation.

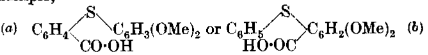
The methoxy-derivatives examined were obtained by the following methods: (1) Condensation of 2-thiolbenzoic acid with a

* The happy analogy of KFHF as a substance similarly constituted was suggested by Professor Robert Robinson in conversation.

methoxy-derivative of benzene in presence of sulphuric acid (J. 1910, **97**, 1290; 1911, **99**, 1353):

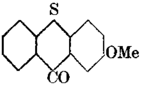


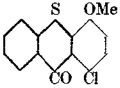
(2) Dehydration of a 2-carboxy-derivative of diphenyl sulphide for example,

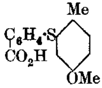


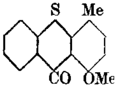
These two types of acid were obtained either (method *a*) from 2-thiol-benzoic acid and a methoxy-halogen derivative of benzene or (method *b*) from phenyl mercaptan and a 2-halogen derivative of a methoxybenzoic acid.

Monomethoxy-derivatives.—Condensation of anisole with 2-thiol-benzoic acid led to a methoxythioxanthone which was evidently the 2-derivative (I), since it was also formed from 4-iodoanisole (method 2*a*). 1-*Chloro*-4-*methoxythioxanthone* (II) was obtained from 4-chloroanisole and 2-thiolbenzoic acid (method 1). The structure assigned to this substance was inferred from the fact that

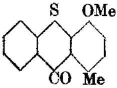

(I.)

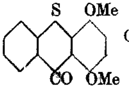

(II.)

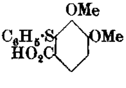

(III.)

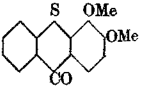

(IV.)

treatment with *p*-toluidine easily replaced the halogen by the toluidino-group (compare Ullmann and Glenck, *Ber.*, 1916, **49**, 2493, 2496). When 2-*iodo*-4-*methoxytoluene*, obtained by usual methods from 2-nitro-*p*-toluidine, was heated with sodium 2-thiol-benzoate in presence of copper acetate, 2′-*carboxy*-5-*methoxy*-2-*methyldiphenyl sulphide* (III) was obtained, and this with sulphuric acid yielded (method 2*a*) 1-*methoxy*-4-*methylthioxanthone* (IV). This substance was entirely different in chemical and physical properties from the product yielded by 4-methoxytoluene and 2-thiol-benzoic acid with sulphuric acid (method 1). Hence the latter material was 4-*methoxy*-1-*methylthioxanthone* (V).


(V.)

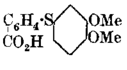

(VI.)


(VII.)

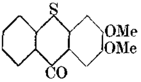

(VIII.)

Dimethoxy-derivatives.—1 : 4-Dimethoxythioxanthone (VI) was

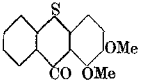
obtained (method 1) from *p*-dimethoxybenzene (Clarke and Smiles, J., 1911, **99**, 1539). When potassium 2-bromoveratrate and potassium phenyl mercaptide were heated together in presence of copper acetate, they yielded 6-carboxy-2 : 3-dimethoxydiphenyl sulphide (VII); this with sulphuric acid (method 2*b*) furnished a dimethoxythioxanthone which must therefore be regarded as the 3 : 4-*derivative* (VIII). Reaction of 4-iodoveratrole with sodium 2-thiolbenzoate gave an acid which was evidently 2′-*carboxy*-3 : 4-*dimethoxydiphenyl sulphide* (IX). Dehydration of this material might lead to either of the two dimethoxythioxanthones (X or XI). In experiment, two such derivatives were isolated as a result of this process, but one of them, later shown to be the 1 : 2-derivative (XI), was produced in only very small amount and was removed from



(IX.)



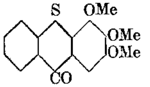
(X.)

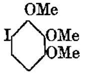


(XI.)

the mixture by means of its more soluble and stable hydrochloride. A similar mixture of these two dimethoxythioxanthones was obtained by condensation of veratrole with 2-thiolbenzoic acid (method 1). Reaction of pyrocatechol with 2-thiolbenzoic acid in sulphuric acid yielded a dihydroxythioxanthone which was easily converted by methylation in aqueous alkaline media into the dimethoxythioxanthone obtained as the chief product from the 2′-carboxy-sulphide (IX) by dehydration. The choice of structure to be assigned to this dihydroxythioxanthone therefore lies between the 2 : 3 and 1 : 2 arrangements (compare X and XI). The former alternative is indicated by the ease with which the substance is methylated and is confirmed by the fact that treatment with boroacetic anhydride did not yield a co-ordinated diacetoborate but merely gave the *diacetoxythioxanthone*. The valuable work of Dimroth (*Ber.*, 1921, **54**, 3020; *Annalen*, 1926, **446**, 97) on the use of this reagent in determining the structure of aromatic hydroxy-ketones has shown that this behaviour is incompatible with the presence of the *o*-hydroxy-group. It may be added that examination of hydroxythioxanthones has confirmed Dimroth's wider experience in other classes of similar hydroxy-ketones and that all the 1-hydroxythioxanthones examined, including 1 : 2-dihydroxy-derivatives, yield stable and characteristic diacetoborates. Hence the related dimethoxy-derivative which forms the chief product when the sulphide (IX) is dehydrated must be the 2 : 3-isomeride (X), leaving for the subordinate product the 1 : 2 structure (XI).

Trimethoxy-derivative.—Reaction of pyrogallol trimethyl ether and 2-thiolbenzoic acid (method 1) gave a trimethoxythioxanthone which had the same melting point as that recorded for the 2 : 3 : 4-derivative prepared by Ullmann and Sone (*Ber.*, 1911, **44**, 2146) from the corresponding trihydroxythioxanthone. Since there were reasons for suspecting that a small quantity of an isomeride might be present in this material, the required 2 : 3 : 4-trimethoxythioxanthone (XII) was obtained from 1-iodo-2 : 3 : 4-trimethoxy-

(XII.) 

 (XIII.)

benzene (XIII) (Graebe and Suter, *Annalen*, 1905, **340**, 222) and 2-thiolbenzoic acid (method 2*a*).

Perchlorates.—Since a perchlorate of thioxanthone is obtained under anhydrous conditions (Gomberg, *Annalen*, 1910, **376**, 211), it is not surprising that most of these methoxy-derivatives yield perchlorates under less stringent conditions. Under the conditions described, perchlorates of normal composition were isolated from all except the 1-chloro-4-methoxy- (II) and 4-methoxy-1-methyl (V) thioxanthones.

Hydrochlorides.—All the methoxy-derivatives examined, except these two 4-methoxy-compounds, dissolve with varying facility in warm concentrated hydrochloric acid, those containing 1-methoxyl being exceptionally soluble compared with the others. The hydrochlorides, isolated from the cooled medium, were too readily hydrolysed to be analysed, but the corresponding chloroplatinates and ferrichlorides of 1 : 4- and 2 : 3-dimethoxythioxanthones were sufficiently stable. These salts of 1 : 4-dimethoxythioxanthone had the normal composition X_2,H_2PtCl_6 and $X,HFeCl_4$, but the 2 : 3-derivative yielded a ferrichloride, $X_2,HFeCl_4$. The formation of hydrochlorides was further examined by reaction with dry hydrogen chloride at atmospheric pressure and temperature; the results are collected in the second column of the following table. The relative stability of the salts of these derivatives was also studied with the aid of the method devised by Baeyer and Villiger (*Ber.*, 1902, **35**, 3020). This process has been used with full recognition of the errors to which it is liable (compare Ziegler and Boye, *Annalen*, 1927, **458**, 229), but with suitable precautions the chief objections to its use were overcome. Column IV of the table gives the volumes (c.c.) of alcohol which were required for decomposition of the halochromic salts formed from equimolecular proportions of the thioxanthone derivatives under standard conditions. Quantitative

accuracy is not claimed for these data; they are recorded as illustrating the approximate stability of the salts of the various derivatives compared with that formed from thioxanthone itself.

I. Derivative.	II. Mols. HCl absorbed.	III. Colour of salts.	IV. C.c. alcohol required.
Thioxanthone	None.	—	7
1-Chloro-4-methoxy-	None.	—	6·5
4-Methoxy-1-methyl-	None.	—	7
2-Methoxy-	HCl absorbed; product unstable.	Orange.	10
3 : 4-Dimethoxy-	HCl absorbed; product unstable.	Orange.	12
2 : 3 : 4-Trimethoxy-	*ca.* 1·5; unstable.	Orange.	10
2 : 3-Dimethoxy-	2HCl.	Orange.	14
1 : 2-Dimethoxy-	*Not examined.*	*Crimson.*	*26*
1 : 4-Dimethoxy-	2HCl.	Crimson.	28
1-Methoxy-4-methyl-	3HCl.	Deep red.	30
1 : 4-Dimethyl-	None.	—	7–8
1 : 4-Dimethoxy-dioxide	*None.*	—	*4–5*
2 : 3-Dimethoxy-dioxide	None.	—	0

The results obtained by these two methods (columns II and IV) are in qualitative agreement. The stability of the salts of these methoxy-derivatives evidently does not primarily depend on the number of methoxy-groups present, but is more readily influenced by their position. The 4-methoxy-group does not favourably influence the basic character of the thioxanthone nucleus, in fact in certain cases the group in question may have an adverse effect; this appears on comparing the behaviour of the 2 : 3-, 2 : 3 : 4-, and 3 : 4-derivatives. Also it is clear that the salts of 1-methoxythioxanthones have exceptional physical properties and are more stable than those formed by other methoxy-derivatives. On comparing the 3 : 4- and 1 : 4-isomerides, the enhanced effect of 1-methoxyl in comparison with 3-methoxyl becomes apparent; and the contrast between 1-methoxy-4-methylthioxanthone and its epimeride is even more striking. Another interesting feature is the inert character of the sulphones derived from the 1 : 4- and 3 : 4-dimethoxythioxanthones. Before a discussion of the structure of these salts and of the remarkable influence of the 1-methoxyl can be profitably undertaken, further evidence is desirable; this is being collected and will be given in a future communication.

Experimental.

2-*Carboxy-derivatives of Diphenyl Sulphide* (2*a* and 2*b*).—2′-*Carboxy-4-methoxydiphenyl sulphide*, $MeO{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$. Amyl alcohol (17 c.c.), containing 2-thiolbenzoic acid (4·9 g.), 4-iodoanisole (7·5 g.), potassium carbonate (4·5 g.), and a little copper acetate, was boiled for 16 hours. After addition of aqueous alkali hydroxide the alcohol was removed by a current of steam, and the filtered

solution mixed with an excess of dilute hydrochloric acid. The required *acid*, which was precipitated (90% yield), separated from acetic acid in needles, m. p. 232° (Found : C, 64·1 ; H, 4·5. $C_{14}H_{12}O_3S$ requires C, 64·6 ; H, 4·6%).

2'-Carboxy-5-methoxy-2-methyldiphenyl sulphide (III). The reduction of 2-nitro-4-methoxytoluene was effected by tin and hydrochloric acid under the usual conditions or by the method described by West (J., 1925, **127**, 494), but the latter gave poor yields. The product obtained by the former method was purified by a current of steam in order to separate a small quantity of a less volatile base (m. p. 112°) containing halogen. This material (compare Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 85) was evidently *chloro-4-methoxy-*o*-toluidine* (Found: C, 55·8; H, 5·6; *M*, 175. $C_8H_{10}ONCl$ requires C, 56·0; H, 5·8%; *M*, 171·5) and appeared to be identical with the substance (m. p. 111°) encountered in this process by Limpach (*Ber.*, 1889, **22**, 791) and described by him as 4-methoxy-*o*-toluidine.

When the diazotised 4-methoxy-*o*-toluidine was treated with potassium iodide under the usual conditions, *2-iodo-4-methoxytoluene* was obtained in good yield. Purified by distillation under atmospheric pressure, it was a pale yellow liquid, b. p. 252—253° (Found : C, 38·7 ; H, 3·5. C_8H_9OI requires C, 38·7 ; H, 3·6%).

Amyl alcohol (17 c.c.), mixed with 2-iodo-4-methoxytoluene (7·9 g.), 2-thiolbenzoic acid (4·9 g.), dry potassium carbonate (4·5 g.), and a little copper acetate, was boiled (16 hours). The usual treatment (*vide supra*) then gave the crude product (75% yield), which was purified from acetic acid. The *substance* (III) formed colourless needles, m. p. 176—177° (Found : C, 65·7 ; H, 5·0. $C_{15}H_{14}O_3S$ requires C, 65·7 ; H, 5·1%).

2'-Carboxy-3 : 4-dimethoxydiphenyl sulphide (IX). 4-Iodoveratrole, obtained from 4-aminoveratrole by the usual method, was condensed with 2-thiolbenzoic acid in boiling amyl alcohol in presence of carbonate and copper acetate. The required *derivative* of diphenyl sulphide separated from acetic acid in plates, m. p. 212—213° (Found: C, 62·2; H, 4·9. $C_{15}H_{14}O_4S$ requires C, 62·1 ; H, 4·8%).

Derivatives of Thioxanthone.—The perchlorates described were obtained by addition of perchloric acid to a benzene solution of the methoxy-derivative concerned which had been saturated with hydrogen chloride, and the precipitated salts were analysed after the usual treatment. The formation and composition of hydrochlorides was examined by submitting the methoxy-derivatives to the action of hydrogen chloride until constant weight had been attained. The approximate relative stabilities of the salts of these thioxanthone derivatives, as indicated by column IV of the table

(p. 867), were studied by the following method. A solution of the sulphate was obtained by adding a mixture (2 c.c.) of sulphuric and acetic acids (1 : 2 by vol.) to a solution of 0·00025 mol. of the thioxanthone in acetic acid (5 c.c.). Alcohol was then added until decomposition of the salt was complete, the end-point being indicated by comparison with solutions of similar dilution without sulphuric acid. In cases where the presence of sulphuric acid caused a permanent change in the colour, titration was continued until the colour was the same as that of a solution of similar composition and "permanent" tint.

2-Methoxythioxanthone (I) was obtained from 2′-carboxy-4-methoxydiphenyl sulphide by treatment (1 hour) with sulphuric acid at 15°. The product, isolated by addition of ice, separated from chloroform in bright yellow needles, m. p. 129°; it was identical with the methoxythioxanthone obtained from anisole and 2-thiolbenzoic acid (J., 1910, **97**, 1296). 2-Hydroxythioxanthone (J., 1928, 3158) was formed in both these methods if solution in sulphuric acid was prolonged. The orange *perchlorate* was isolated in the manner described (Found: $HClO_4$, 29·1. $C_{14}H_{10}O_2S,HClO_4$ requires $HClO_4$, 29·3%). This thioxanthone was slightly soluble in hot concentrated hydrochloric acid and absorbed dry hydrogen chloride, but the product of the latter process was too unstable to permit quantitative examination.

1-*Chloro-4-methoxythioxanthone* (II). A mixture of 2-thiolbenzoic acid (6 g.), sulphuric acid (150 c.c.), and 4-chloroanisole (16 g.) was stirred (1½ hours). After isolation by addition of ice and treatment with alkali to remove acids and phenols, the *product* (8 g.) crystallised from acetone in pale yellow needles, m. p. 196° (Found: C, 60·7; H, 3·4; Cl, 12·5. $C_{14}H_9O_2ClS$ requires C, 60·7; H, 3·3; Cl, 12·8%). The substance did not yield a perchlorate or hydrochloride by the methods described. When a solution in *p*-toluidine containing potassium acetate and a little copper acetate was boiled (15 mins.), the halogen was replaced by the *p*-toluidino-group (compare Ullmann and Glenck, *loc. cit.*). 1-p-*Toluidino-4-methoxythioxanthone* separated from alcohol in red needles, m. p. 133°, which yielded a yellow hydrochloride (Found: C, 72·6; H, 5·2. $C_{21}H_{17}O_2NS$ requires C, 72·6; H, 4·9%).

4-*Methoxy-1-methylthioxanthone* (V). Condensation of 4-methoxytoluene and 2-thiolbenzoic acid was effected as described in the case of 1-chloro-4-methoxythioxanthone. The *substance* separated from alcohol in pale yellow needles, m. p. 162°, was insoluble in warm concentrated hydrochloric acid, and did not yield a perchlorate under the conditions described (Found: C, 70·0; H, 4·8. $C_{15}H_{12}O_2S$ requires C, 70·3; H, 4·7%).

1-*Methoxy-4-methylthioxanthone* (IV). A solution of 2′-carboxy-3 methoxy-6-methyldiphenyl sulphide (III) in ten times its weight o cooled sulphuric acid was stirred (1 hour). After addition of ice a red sulphate separated, but with excess of water this was hydrolysed yielding (50%) the required *thioxanthone*. This separated from ho alcohol in bright yellow needles, m. p. 128° (Found : C, 70·2 ; H, 4·7 $C_{15}H_{12}O_2S$ requires C, 70·3 ; H, 4·7%). The substance was solubl in warm hydrochloric acid and absorbed dry hydrogen chloride forming a red *hydrochloride* (Found : HCl, 29·9. $C_{15}H_{12}O_2S,3HC$ requires HCl, 29·9%). The crimson *perchlorate* was relatively stable being slowly hydrolysed by cold water (Found : $HClO_4$, 28·2 $C_{15}H_{12}O_2S,HClO_4$ requires $HClO_4$, 28·1%).

1 : 4-Dimethoxythioxanthone (VI) prepared by the method of Clarke and Smiles (*loc. cit.*) was readily soluble in concentrated hydrochloric acid ; the hydrochloride separated in crimson needles from the cooled solution. With the dry reagent a *dihydrochloride* was formed (Found : HCl, 21·2. $C_{15}H_{12}O_3S,2HCl$ requires HCl, 21·1%). The *chloroplatinate* was obtained as sparingly soluble, deep red needles by adding chloroplatinic acid to a solution of the hydrochloride in alcohol [Found : Pt, 20·3. $(C_{15}H_{12}O_3S)_2,H_2PtCl_6$ requires Pt, 20·4%]. The *ferrichloride* separated in red needles when a solution of the hydrochloride in acetic acid was mixed with ferric chloride in the same solvent (Found : Fe, 11·6. $C_{15}H_{12}O_3S,HFeCl_4$ requires Fe, 11·9%). The crimson *perchlorate* was obtained in the usual manner (Found : $HClO_4$, 26·8. $C_{15}H_{12}O_3S,HClO_4$ requires $HClO_4$, 27·0%).

3 : 4-*Dimethoxythioxanthone* (VIII). 2-Bromoveratric acid (3·4 g.), thiophenol (1·8 g.), potassium carbonate (1·8 g.), and a little copper acetate were kept in boiling amyl alcohol (3½ hours). The required acid (VII) was isolated by the usual method (*vide supra*) in the crystalline state ; it was converted by solution in sulphuric acid (1 hour ; 15°) into the required *thioxanthone*. This was isolated in the usual manner ; it separated from hot alcohol in pale yellow needles, m. p. 185° (Found : C, 66·0 ; H, 4·5. $C_{15}H_{12}O_3S$ requires C, 66·2 ; H, 4·4%). The orange *perchlorate* was obtained in the usual way (Found : $HClO_4$, 26·9. $C_{15}H_{12}O_3S,HClO_4$ requires $HClO_4$, 27·0%), but the hydrochloride, evidently formed by reaction with dry hydrogen chloride, was too unstable for examination. This dimethoxythioxanthone was very slightly soluble in warm hydrochloric acid.

2 : 3-*Dihydroxythioxanthone* (compare X). Pyrocatechol (3 g.) was gradually added to cooled stirred sulphuric acid (40 c.c.) which contained 2-thiolbenzoic acid (2 g.). The solid which separated after addition of ice was collected and dissolved in aqueous alkali

hydroxide; the required substance was liberated from this solution by carbonic acid. It separated from acetic acid or alcohol in orange needles which firmly retained these solvents; it was brought to analysis as the *diacetyl* derivative, pale yellow needles, m. p. 191°, from alcohol (Found: C, 61·9; H, 3·8. $C_{17}H_{12}O_5S$ requires C, 62·2; H, 3·6%). Oxidation of the hydroxythioxanthone yielded the dioxide (J., 1928, 3159), and aqueous alkaline methylation furnished the dimethoxy-derivative, m. p. 172°. The substance gave a yellow solution in boiling acetic anhydride which contained boroacetic anhydride (compare Dimroth, *loc. cit.*): when this was cooled, the diacetyl derivative separated in the crystalline state; it was identified with a sample prepared by another method. The formation of a boroacetate was not observed. In contrast with this behaviour, that of 1 : 4-dihydroxythioxanthone is described. With the reagent in question, this substance furnished a crimson boroacetate which was decomposed by boiling water, yielding 1-*hydroxy*-4-*acetoxythioxanthone*, which formed yellow needles, m. p. 171°, from alcohol (Found: C, 62·8; H, 3·6. $C_{15}H_{10}O_4S$ requires C, 62·9; H, 3·5%). For comparison, 1 : 4-*diacetoxythioxanthone* was prepared in the usual manner; it formed yellow needles, m. p. 168°, from alcohol (Found: C, 61·7; H, 3·6. $C_{17}H_{12}O_5S$ requires C, 62·2; H, 3·6%). A mixture of this with the monoacetyl derivative melted indistinctly below 150°.

2 : 3-*Dimethoxythioxanthone* (X). 2′-Carboxy-3 : 4-dimethoxy-diphenyl sulphide (IX) was converted into the thioxanthone by solution in sulphuric acid. The product, isolated in the usual way, contained two substances, one of which was present in only small quantity and gave a more soluble, crimson hydrochloride. The material was triturated with concentrated hydrochloric acid, the deep red filtrate being set aside. The sparingly soluble, yellow hydrochloride was treated with this reagent until the red salt was removed. The residue was then decomposed with water and the liberated *thioxanthone*, purified from alcohol, was obtained in pale yellow needles, m. p. 172° (Found: C, 65·9; H, 4·4. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4%). The substance was sparingly soluble in concentrated hydrochloric acid. The orange *hydrochloride* was obtained by reaction with hydrogen chloride (Found: HCl, 21·2. $C_{15}H_{12}O_3S,2HCl$ requires HCl, 21·2%). When a solution of ferric chloride in acetic acid was added to a solution of the thioxanthone in this medium which had been saturated with hydrogen chloride, the *ferrichloride* separated in orange needles [Found: Fe, 7·4. $(C_{15}H_{12}O_3S)_2,HFeCl_4$ requires Fe, 7·5%]. Under conditions which provided a large excess of ferric chloride, a chocolate-brown *ferrichloride* separated in plates (Found: Fe, 11·9. $C_{15}H_{12}O_3S,HFeCl_4$

requires Fe, 11·9%). This dimethoxythioxanthone was also prepared by (1) aqueous alkaline methylation of the dihydroxythioxanthone obtained from pyrocatechol and 2-thiolbenzoic acid in sulphuric acid and (2) condensation of veratrole with 2-thiolbenzoic acid in the same medium. The latter method was the more convenient (yield, 30%), but the product contained a small quantity of the 1 : 2-dimethoxy-derivative, which was removed by treatment with hydrochloric acid.

1 : 2-*Dimethoxythioxanthone* (XI) was contained in the red solution of the more soluble hydrochloride removed during purification of the 2 : 3-derivative as described in the previous paragraph. The thioxanthone was recovered from this by treatment with water, the process of fractionating the hydrochloride being repeated; finally the thioxanthone was obtained in yellow needles, m. p. 143—144°, from acetic acid (Found: C, 66·6; H, 4·7. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4%). The substance gave a crimson hydrochloride and perchlorate.

2 : 3 : 4-Trimethoxythioxanthone (XII). *A mixture of 2-thiol*benzoic acid (3 g.), 1 : 2 : 3-trimethoxybenzene (4 g.), and sulphuric acid (60 c.c.) was warmed until a clear solution was obtained. The product, isolated after the usual treatment, separated from alcohol in pale yellow needles, m. p. 150° (Ullmann and Sone record m. p. 153—154° for the methylation product of 2 : 3 : 4-trihydroxythioxanthone). Since this mode of preparation does not exclude the presence of the 1 : 2 : 3-isomeride as an impurity, the material required for further examination was prepared from 1-iodo-2 : 3 : 4-trimethoxybenzene (Graebe and Suter, *loc. cit.*) and 2-thiolbenzoic acid in presence of alkali carbonate and copper acetate by the usual method. The carboxylic acid obtained was dissolved in warm sulphuric acid (15 mins.), from which ice precipitated the 2 : 3 : 4-trimethoxythioxanthone. After purification this had m. p. 150° and was identical with the material obtained by the other method (Found: C, 63·8; H, 4·8. Calc.: C, 63·6; H, 4·6%). The substance was sparingly soluble in warm hydrochloric acid, and the orange *salt* prepared with the dry reagent was unstable, losing hydrogen chloride during manipulation (Found: HCl, 16·5. $C_{16}H_{14}O_4S,2HCl$ requires HCl, 19·5%). The orange *perchlorate* had the normal composition (Found: $HClO_4$, 25·0. $C_{16}H_{14}O_4S,HClO_4$ requires $HClO_4$, 24·9%).

KING'S COLLEGE, LONDON. [*Received, February 26th, 1929.*]

CXIV.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part V. The Constitution of Squalene as deduced from its Degradation Products.*

By ISIDOR MORRIS HEILBRON, WILLIAM MORGAN OWENS, and IAN ALEXANDER SIMPSON.

SINCE our previous publication on this subject (Heilbron, Kamm, and Owens, J., 1926, 1630), in which reference was made to a preliminary communication by André and Canal (*Compt. rend.*, 1925, **181**, 612), a detailed account of their work has appeared (*Ann. Chim.*, 1927, **7**, 69). These authors seemingly hold the view that either squalene is not a single substance or, if it is, its formula is best represented as $C_{28}H_{46}$ (or possibly $C_{27}H_{44}$) but not as that of a dihydrotriterpene, $C_{30}H_{50}$. Criticism of our results is based on the ground that analyses of the hydrohalides are insufficient to allow of a decision being made with regard to the constitution of the hydrocarbon owing to the salts being incompletely saturated. If this be so, it is certainly a striking coincidence not only that the majority of André and Canal's analytical values for both the hydrochlorides and the hydrobromides indicate the $C_{30}H_{50}$ formulation, but that in more than fifty analyses of the isomeric hydrochlorides, prepared in these laboratories from squalene obtained from various sources, the percentages of carbon, hydrogen, and halogen are in every case in agreement with this formula (compare also Tsujimoto, *J. Ind. Eng. Chem.*, 1916, **8**, 889). The results obtained by André and Canal, for details of which their original paper must be consulted, are so conflicting that criticism is rendered difficult. That they themselves feel some uneasiness regarding their own inferences is apparent from a further communication (*Bull. Soc. chim.*, 1928, **44**, 371) in which they seemingly come to our conclusion (Heilbron, Kamm, and Owens, *loc. cit.*) that the two hydrochlorides of different melting point are actually isomerides and are not salts of neighbouring homologues. As regards the formula $C_{28}H_{46}$, this is now left an open question.

We would point out that the dihydrotriterpene structure for squalene was not advanced *solely* on the analytical values of the hydrohalide salts: other factors were taken into consideration. Of these, its typical terpene character as evidenced by (*a*) the pyrogenic decomposition products, (*b*) the ease with which it undergoes ring closure, and (*c*) the substances obtained by the action of ozone (Majima and Kubota, *Jap. J. Chem.*, 1922, **1**, 19), may be cited.

The present communication deals with work primarily undertaken with the idea of proving that under all methods of attack squalene yields decomposition products typical of those to be anticipated from a triterpene hydrocarbon. The results actually obtained have, however, enabled us to ascribe definite structural formulæ to the isomeric hydrocarbons of which it is composed.

In the first place we have repeated our previous work on the distillation of squalene, using larger quantities of the hydrocarbon and examining especially the low-boiling fraction from which Chapman (J., 1918, **113**, 458; 1923, **123**, 769) obtained a cyclic hydrocarbon similar in physical characteristics to *cyclo*dihydromyrcene (compare also Majima and Kubota, *loc. cit.*). Fractions agreeing closely with those obtained by these authors have been isolated, but we consider them to be constant-boiling mixtures rather than individual substances.

We have also repeated the hot-wire method of decomposition employed by Chapman (J., 1923, **123**, 769) and here again our experiments have failed to confirm the existence of a single substance such as the diolefinic hydrocarbon, heparene ($C_{10}H_{18}$), isolated by him. Indications of the presence of an unsaturated open-chain terpene (myrcene ?) have been furnished by an experiment in which the monoterpene fraction was boiled with formic acid, whereby a high-boiling hydrocarbon closely resembling dimyrcene in physical characteristics was separated (Semmler and Jones, *Ber.*, 1913, **46**, 1566). Its appearance in this manner is obviously the result of the polymerisation of some constituent of lower molecular weight in the original mixture.

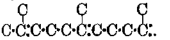
In the hope of being able definitely to identify some particular monoterpene, we made attempts with each fraction of seemingly homogeneous nature to isolate a solid derivative, such as the bromide or the hydrochloride, but only uninviting oily products were obtained.

Action of Ozone upon Squalene.—By the action of ozone upon squalene, Majima and Kubota (*loc. cit.*) readily obtained a hexaozonide from which carbon dioxide, acetone, acetone peroxide, formaldehyde, formic acid, succinic acid and lævulic acid were produced on decomposition with water. In addition, two acidic substances were isolated in small quantity, to which the formulæ $C_6H_{10}O_5$ and $C_8H_{14}O_6$ were ascribed, without, however, their structures being determined. We have repeated this investigation and have not only confirmed the formation of all the above products, but ascertained that the two supposed acids are in reality peroxides. The compound of lower molecular weight, m. p. 195°, has actually the formula $C_5H_8O_4$ and is identical with lævulic aldehyde peroxide

(compare Harries, *Ber.*, 1905, **38**, 1201): the substance $C_8H_{14}O_6$, m. p. 136°, appears to be a complex peroxide of methylheptenone.

Oxidation of Squalene with Potassium Permanganate.—The action of potassium permanganate upon squalene was examined by Chapman (J., 1923, **123**, 769), who, however, was unable to isolate any derivatives likely to throw light on its constitution. On treatment with alkaline permanganate the formation of "a little acetone together with a trace of some fragrant ketone" was noted, but the bulk of the hydrocarbon either remained unattacked or was completely destroyed according to the conditions employed.

The results obtained by us substantially confirm these findings, but, by treatment of squalene in acetone solution with solid potassium permanganate at room temperature, two ketones have been isolated in minute amount, one of which we have definitely characterised as dihydro-ψ-ionone (geranylacetone). The formation of this ketone adds an important link to the evidence of the terpenoid nature of squalene, proving as it does the presence of the carbon skeleton



The other ketone is almost certainly methylheptenone, and its presence accords well with the isolation of the $C_8H_{14}O_6$ peroxide. An acid portion has also been obtained from which succinic acid has been separated.

The greater part of the squalene was recovered unchanged and was further treated with an excess of potassium permanganate in the heat. Even under these drastic conditions about 40% of the squalene was unacted upon, the remainder being completely burnt to carbon dioxide. The residual squalene yielded a hydrochloride (m. p. 105—116°) from which, after *one* crystallisation, mainly the high-melting isomeride was obtained. The ready formation of this hydrochloride, which is only slowly accumulated from untreated squalene, adds further support to our contention (Heilbron, Kamm, and Owens, *loc. cit.*) that squalene is a mixture of two isomerides and suggests that one isomeride is more readily broken down than the other.

Oxidation of Squalene with Chromyl Chloride.—The additive products obtained by treating a solution of squalene in carbon disulphide with chromyl chloride in the same solvent furnished, on decomposition with water, small amounts of formaldehyde, acetaldehyde and succinic acid, together with much unworkable resinous material. In the last respect the results are similar to those recorded by Chapman (*Analyst*, 1927, **52**, 622) but, contrary to the findings of this author, the completely saturated addition product was obtained with twelve molecules of chromyl chloride instead of eight.

Squalene Dodecabromide.—As early as 1916, Tsujimoto (*J. Ind.*

Eng. Chem., **8**, 894) found that squalene formed an addition compound with bromine, m. p. 170—176° (decomp.), to which he ascribed the formula $C_{30}H_{50}Br_{12}$. Chapman (J., 1917, **111**, 63) also has described a dodecabromide of spinacene, m. p. 185°, which he found was divisible into two portions differing in solubility but having the same composition ($C_{30}H_{50}Br_{12}$). In a further paper (J., 1918, **113**, 458) this author commented on the fact that the purified dodecabromide was the sole exception to his amended formula for spinacene ($C_{29}H_{48}$), but ultimately, by crystallisation of the less soluble portion from a mixture of tetrachloroethane and alcohol, a compound conforming to this formula was obtained (J., 1923, **123**, 770).

In the present work, squalene from several sources was carefully brominated at − 25°, and the colourless bromide separated into a high- and a low-melting product by means of ethyl acetate. The latter, which was the more soluble, rapidly darkened in moist air and, owing to decomposition, could not be recrystallised. On the other hand, the high-melting, insoluble dodecabromide (m. p. 198°) was stable and gave analytical values definitely fixing its formula as $C_{30}H_{50}Br_{12}$.

Discussion of Results.

Although we have failed to obtain any direct information, leading to the elucidation of the structure of squalene, from the results of our examination of the low-boiling pyrogenic decomposition products, there can be little doubt that these constitute a complex mixture of mono- and dihydromono-terpenes. That a mixture of this nature should exist is in strict accord with our view that squalene is a dihydrotriterpene, and finds confirmation both in the work previously carried out (Part I) and in our isolation of methylheptenone and dihydro-ψ-ionone. The formation of these ketones together with the appearance of acetone, lævulic aldehyde and lævulic acid among the decomposition products of the ozonide affords striking confirmation of our previously suggested structure (Heilbron, Kamm, and Owens, *loc. cit.*) for one form of squalene (I).

(I.) $CMe_2{:}CH{\cdot}CH_2{\cdot}[CH_2{\cdot}CMe{:}CH{\cdot}CH_2]_4{\cdot}CH_2{\cdot}CMe{:}CHMe$

(II.) $CMe_2{:}CH{\cdot}CH_2{\cdot}[CH_2{\cdot}C({:}CH_2){\cdot}CH_2{\cdot}CH_2]_4{\cdot}CH_2{\cdot}CMe{:}CHMe$

Such a structure, however, fails to account for the formation of carbon dioxide (8·5%), formaldehyde, formic acid and succinic acid (28%) in the same decomposition. We are therefore forced to the conclusion that at least one isomeride must exist, and for this we suggest formula (II), a structure which has already been deduced from the hydrogenation of squalene (Heilbron, Hilditch, and Kamm, J., 1926, 3131).

The formation of formaldehyde and acetaldehyde in the chromyl chloride reaction is also in harmony with the above formulations, for, whereas the former obviously arises from the $>C:CH_2$ gronp (formula II), the latter is produced by scission at the double bond of the terminal group CMe:CHMe common to both structures.

The weight of the oxidation products isolated by us from the ozone treatment accounts for fully 90% of the squalene used (Majima and Kuhota obtained a somewhat higher percentage)—a fact which, taken in conjunction with the other evidence now provided, appears to us to refute André and Canal's contention that squalene has a molecular formula other than $C_{30}H_{50}$.

EXPERIMENTAL.

Squalene from the liver oil of *Centrophorus granulosus* was originally employed, but later the hydrocarbon was extracted from *Spinax niger* and *Scymnorhinus lichia*. In no case, however, was any difference observed in the characteristics of the pure hydrocarbon, which was worked up by the distillation process previously described (Heilbron, Kamm, and Owens, *loc. cit.*).

Decomposition of Squalene by Heat.—The hydrocarbon was distilled in portions not exceeding 400 g. at 300—350 mm. in an atmosphere of nitrogen. Excluding the hemiterpene fraction, which has previously been shown to consist mainly of the amylene CMe_2:CHMe, a typical decomposition yielded a clear, golden-yellow, mobile liquid (yield, 70%). The residne consisted of a dark brown, very viscous liquid which hardened to a horny mass on standing. The distillate was roughly fractionated at 20 mm. in an atmosphere of nitrogen and the monoterpene portion ($n_D^{15.5°}$ 1·4634) boiling between 40° and 100° (30% of the total) was collected and subjected to careful fractional distillation. No evidence of the presence of any homogeneous fraction was obtained, the temperature rising gradually throughout the whole operation. The most abundant fraction, b. p. 60—63°/15 mm. (Majima and Kubota find 64—66°/18 mm. for their hydrocarbon similar to *cyclo*dihydromyrcene), was obtained as a pale yellow liquid (30%), $d_4^{17.5°}$ 0·8225, $n_D^{20°}$ 1·4619 (Found: C, 87·5; H, 12·4; iodine value, 316. $C_{10}H_{16}|_3^{=}$ requires C, 88·2; H, 11·8%; iodine value, 373. $C_{10}H_{18}|_1^{=}$ requires C, 87·0; H, 13·0%; iodine value, 184). The non-homogeneous character of the fraction indicated by the analytical data was confirmed by refractionation from a Willstätter flask; the seemingly constant-boiling liquid then distilled over a much wider range (162—177°/740 mm.) and the physical constants of the collected fractions changed uniformly with rise in boiling point.

Decolorisation of the Monoterpene Fraction.—As all the distillates

obtained by the above method of decomposition were of a bright yellow colour, appropriate fractions from different experiments were mixed together and thrice distilled over sodium, whereby colourless pleasant-smelling, mobile liquids resulted. Of the larger fractions the following are of especial interest, as they closely approximate in physical characteristics to those recorded both by Chapman and by Majima and Kubota (*locc. cit.*).

(1) B. p. 167—170°/759 mm., $d_{16^\circ}^{16^\circ}$ 0·8188, $n_D^{20^\circ}$ 1·4589 (Found: C, 87·4; H, 12·4%; bromine value, 138; iodine value, 270 $C_{10}H_{18}|^=$ requires bromine value, 116; iodine value, 184).

(2) B. p. 174—176°/759 mm., $d_{16^\circ}^{16^\circ}$ 0·8262, $n_D^{20^\circ}$ 1·4624 (Found C, 87·3; H, 12·7%; bromine value, 148; iodine value, 263).

The bromine values are in fair agreement with the figures given by Chapman (J., 1918, **113**, 464) for the mono-olefinic cyclic hydrocarbon obtained by the decomposition of squalene (spinacene) in the presence of sodium. On the other hand, the iodine absorption values found by us correspond to the addition of three atoms of iodine per molecule of hydrocarbon. It is thus clear that evidence based on either bromine or iodine absorption cannot be relied upon as a sure criterion of structure. Attention must also be drawn to the results of ultimate analysis. Whereas both the above-mentioned authors give analytical figures in agreement with $C_{10}H_{18}$, our values for carbon (over 15 analyses on different fractions) invariably *correspond to the requirements of a hydrocarbon mixture of* $C_{10}H_{16}$ and $C_{10}H_{18}$ molecules, the relative proportion of which remains almost constant no matter how far the degree of fractionation is carried.

Hot-wire Decomposition of Squalene.—This was carried out according to Chapman's directions (J., 1923, **123**, 769) in a specially constructed Jena flask containing in the neck a mesh of fine platinum wire which was maintained at a dull red heat during the distillation process by means of an electric current. Squalene in three batches of 140 g. was distilled under a pressure of 45—50 mm. The bright yellow, mobile distillate (273 g.) was divided into two portions and worked up (*a*) by direct fractional distillation and (*b*) by steam distillation.

(a) *Fractional distillation.* The crude distillate was separated into mono-, sesqui- and higher terpene fractions. The monoterpene fraction was examined in great detail but gave the same indefinite fractions as were obtained by the direct pyrogenic decomposition.

(b) *Steam-volatile portion* (42 g. from 133 g. of crude material). Contrary to Chapman's finding (*loc. cit.*), here again we failed to isolate any definite major portion on fractionation, the boiling point rising continuously throughout the distillation (110—171° at the

ordinary pressure). A fraction (10 g.), b. p. 165—171°/755 mm., was ultimately collected as a bright yellow liquid, $d_{15^\circ}^{15^\circ}$ 0·8092, $n_D^{20^\circ}$ 1·4610 (Found: C, 87·4; H, 12·4%; iodine value, 345, 355). The physical constants agree with those given for heparene ($C_{10}H_{18}|\overline{\overline{2}}$), but the yellow colour is completely removed on distillation over sodium and cannot be attributed to a definite structural arrangement of the fraction as a whole.

Action of Formic Acid.—A fraction boiling between 60° and 100°/20 mm. (20 g.) was heated for 24 hours with 99% formic acid (25 g.) on a steam-bath. The deep purple solution was diluted with water, rendered alkaline with sodium carbonate, and extracted with ether. After removal of the solvent from the dried extract, the brown oil was fractionally distilled as follows: (*a*) 160—170°/759 mm. (2·5 g.); (*b*) 171—176°/759 mm. (4 g.), $d_{20^\circ}^{20^\circ}$ 0·8337, $n_D^{20^\circ}$ 1·4582; (*c*) 60—85°/3 mm. (0·5 g.); (*d*) 125—130°/3 mm. (4 g.), $d_{20^\circ}^{20^\circ}$ 0·9098, $n_D^{20^\circ}$ 1·4998. The last fraction was obtained as a viscous yellow liquid having the typical characteristics of a diterpene (Found for fraction *d*: C, 87·8; H, 12·0. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%).

Preparation of Squalene Hexaozonide.—A stream of oxygen containing approximately 5% by volume of ozone was passed at the rate of 6—8 litres per hour through a solution of squalene (30 g.) in dry chloroform (120 g.) maintained at 0°, until excess of ozone was detected at the outlet of the apparatus (72 hours). The solvent was carefully removed below 35° under reduced pressure so as to avoid risk of explosion due to the unstable nature of the hexaozonide. The deposition of crystals of succinic acid from the chloroform solution of the ozonide, as described by Majima and Kubota (*loc. cit.*), was only observed on two occasions. The acid was identified by direct comparison with an authentic specimen of succinic acid, the mixture melting at 179—181°. The ozonide was taken up in dry ether and reprecipitated with light petroleum. The supernatant liquid was decanted and the remaining traces of volatile solvent were removed under reduced pressure. The ozonide formed a colourless viscous syrup (yield, 48 g.).

Decomposition of Squalene Hexaozonide.—This was carried out exactly as described by Majima and Kubota, but it was found difficult to isolate the acetone peroxide in the quantity mentioned by these authors. It was further observed that, if the ozonisation was carried out at room temperature, a larger proportion of lævulic acid was formed at the expense of the two supposed acids, thus pointing to some definite relationship between them. Acetone and carbon dioxide were readily identified, the former being isolated as its semicarbazone (2·5 g.), m. p. 186—187°, and the latter estimated as barium carbonate (equivalent to 2·5 g. of carbon dioxide).

Among the products volatile in steam, acetone peroxide, m. p. 132—134°, was isolated as a crystalline deposit (0·5 g.), and the presence of lævulic aldehyde was detected by the preparation of its phenylmethyldihydropyridazine, m. p. 194—196°. Formic acid was also readily identified. The residual solution obtained after steam distillation was worked up exactly as described by Majima and Kubota and succinic acid (8·4 g.), lævulic acid (11·0 g.), and an alkali-soluble, waxy solid consisting of a mixture of the two unknown "acids" of these authors (3·5 g.) were isolated. These "acids" were separated by boiling benzene, in which the higher-melting compound was almost insoluble, and each was purified by repeated crystallisation from water. *Lævulic aldehyde peroxide* was obtained in colourless needles, m. p. 195° (literature values, 190° to 196°), readily soluble in boiling water, insoluble in benzene [Found: (micro.) C, 45·6; H, 6·3. Calc. for $C_5H_8O_4$: C, 45·4; H, 6·1%]. The substance liberates iodine from dilute potassium iodide solution in the cold and also reduces Fehling's solution. When the peroxide is boiled for 12 hours with water, a clear solution is formed; on treatment with a dilute acetic acid solution of *p*-nitrophenylhydrazine, the *p*-nitrophenylhydrazone of lævulic acid is deposited, m. p. 174—175°.

Methylheptenone peroxide (?) crystallises from boiling water in colourless plates, m. p. 136° (Majima and Kubota give 132—134°) (Found: C, 46·5, 46·5; H, 7·3, 6·9. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8%).

On being heated with water in a closed tube for 8 hours at 140°, the peroxide decomposes, giving a colourless solution devoid of aldehydic reactions and acid to methyl-orange. Lævulic acid *p*-nitrophenylhydrazone, m. p. 169—170°, was isolated from the solution in the usual manner and identified by the melting point, 171—173°, of a mixture with an authentic specimen (m. p. 173—174°).

Oxidation of Squalene with Potassium Permanganate.—A solution of squalene (200 g.) in carefully purified acetone (400 g.) was treated at room temperature with continuous stirring with finely powdered potassium permanganate (300 g.), added in small quantities during 18 hours. The mixture was diluted with water, sulphur dioxide passed into the solution to remove manganese dioxide, and the whole repeatedly extracted with ether. The ethereal solution was separated into acid and neutral portions by extraction with dilute sodium carbonate solution.

Succinic acid. After concentration the alkaline solution was made acid. The precipitated solid crystallised from ethyl acetate in colourless crystals, m. p. 185°, which were identified as succinic acid (melting point of a mixture).

Neutral portion. The ethereal extract, after drying and removal of solvent, was fractionally distilled and yielded a small fraction, b. p. 90—95°/18 mm. The greater portion of the distillate consisted of unchanged squalene, which was again treated with an excess of potassium permanganate in *boiling* acetone solution in presence of magnesium sulphate until all action had ceased. Despite the drastic conditions employed, about 40% of the squalene was recovered, the remainder having been completely burnt to carbon dioxide. The recovered squalene ($n_D^{20°}$ 1·4980) yielded a crude hydrochloride, m. p. 105—116°, which after one recrystallisation from hot ethyl acetate, gave mainly the high-melting squalene hydrochloride (m. p. 121—125°).

Dihydro-ψ-ionone. The low-boiling product had a pleasant pear-like odour (compare Chapman, J., 1923, **123**, 771) and reacted with semicarbazide acetate. The crude semicarbazone (2 g.) was taken up in light petroleum and separated from a small insoluble residue. The filtrate slowly deposited a colourless solid, which was recrystallised from aqueous methyl alcohol. The pure semicarbazone, m. p. 95°, was identified as dihydro-ψ-ionone semicarbazone by comparison with a synthetic specimen prepared from geraniol according to Forster and Cardwell's method (J., 1913, **103**, 1341) [Found: (micro.) C, 67·0; H, 9·9; N, 17·0, 16·8; *M*, 273. Calc. for $C_{14}H_{25}ON_3$: C, 66·9; H, 10·0; N, 16·7%; *M*, 251].

Methylheptenone. The portion insoluble in the light petroleum was dissolved in benzene, from which solution it separated as a colourless microcrystalline solid, m. p. 129—131°, on addition of light petroleum. The properties of this semicarbazone are in fair agreement with those given in the literature (Tiemann and Kruger, *Ber.*, 1895, **28**, 2124) for methylheptenone semicarbazone, which is described as a colourless solid, m. p. 136—138°, difficultly soluble in light petroleum and soluble in benzene. Unfortunately, insufficiency of material precluded further purification and more definite characterisation (Found: N, 22·6. Calc. for $C_9H_{17}ON_3$: N, 22·9%).

Action of Chromyl Chloride upon Squalene.—A 10% solution of chromyl chloride (12 mols.) in dry carbon disulphide was added in small portions at a time and with vigorous shaking to a solution of squalene (24 g.) in the same solvent. The reaction, which was completed in 7 hours, was carried out at −15°. The resultant dark brownish-green precipitate was repeatedly washed with dry carbon disulphide. The filtrate was practically free from chromyl chloride. The addition compound was decomposed with iced water, and the aqueous liquor distilled from a steam-bath, a fraction, b. p. 60—80°, being collected and gaseous material absorbed in water. The

neutral aqueous solution obtained showed strong reducing properties and the presence of formaldehyde was readily detected by means of the Schryver reagent. The solution was carefully oxidised with potassium permanganate (0·5% solution) and evaporated to dryness. On extraction of the resultant solid with hot absolute alcohol, potassium acetate was removed, thus proving that acetaldehyde *must also have been present in the oxidised material.* An examination of the fraction of b. p. 60—80° revealed the presence of acetone, which was isolated both as the *p*-nitrophenylhydrazone (m. p. 148°) and as the semicarbazone (m. p. 187°).

The residue in the flask was separated into acid and neutral portions. From the former, a small amount of succinic acid was obtained; the latter, which consisted of a heavy resinous oil, resisted all attempts at purification.

Squalene Dodecabromide.—A solution of squalene (20 g.) in sodium-dried ether (150 c.c.) was treated at −25° with a solution of dry bromine in ether (90 g. in 200 c.c.). In 30 minutes a colourless crystalline solid separated which, after drying, darkened at 160° and melted at 185° (decomp.). A further crop was obtained by evaporating the filtrate under reduced pressure and triturating the resultant sticky yellow solid with ethyl acetate (total yield, 80%). The bromide can also be prepared directly from the crude liver oil, the product being somewhat darker in colour, but the total yield remains about the same.

Analysis of the crude product. (A) From squalene obtained from *Centrophorus granulosus*: Found, Br, 69·5%. (B) From *Scymnorhinus licia*: Found, C, 26·8, 26·8; H, 3·6, 3·8% ($C_{28}H_{46}Br_{12}$ requires C, 25·0; H, 3·4; Br, 71·6%. $C_{29}H_{48}Br_{12}$ requires C, 25·7; H, 3·5; Br, 70·8%. $C_{30}H_{50}Br_{12}$ requires C, 26·3; H, 3·6; Br, 70·1%. $C_{31}H_{52}Br_{12}$ requires C, 26·9; H, 3·8; Br, 69·3%).

Isolation of the bromide, m. p. 198°. The crude bromide (30 g.) was boiled with ethyl acetate (200 g.), and the soluble portion removed by rapid filtration under pressure. The insoluble residue was repeatedly washed with boiling ethyl acetate until a sample of the filtrate left no deposit on evaporation. The dodecabromide formed a hard, microcrystalline, colourless solid, m. p. 198° (decomp. but without previous darkening), insoluble in the common organic solvents but soluble to some extent in pyridine, tetrachloroethane and xylene [Found (squalene from *Centrophorus granulosus*): C, 26·2, 26·3; H, 3·4, 3·4; Br, 69·9%. Found (squalene from *Scymnorhinus lichia*): C, 26·4, 26·4; H, 3·7, 3·8%].

Soluble bromide. The brown ethyl acetate filtrate deposited on cooling a solid, m. p. 178°, which decomposed to a marked extent in moist air with a lowering of m. p. to 174° (unsharp). Attempts

to purify this were unsuccessful owing to obvious decomposition in the boiling solvent (Found on immediate analysis: C, 26·7; H, 3·8; Br, 69·5%. Found after 14 days: C, 28·5; H, 3·8%).

In conclusion we desire to express our thanks to Mr. E. B. Parkes, M.Sc., for help in the examination of the squalene dodecabromide, and to the Food Investigation Board for a grant which has enabled this investigation to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, March 9th,* 1929.]

CXV.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part VI. The Constitution of Squalene as deduced from a Study of the Decahydrosqualenes.*

By ISIDOR MORRIS HEILBRON and ALBERT THOMPSON.

ALTHOUGH the structure of squalene has been largely elucidated as a result of the work described in former communications (especially Part V, preceding paper), additional evidence would nevertheless be welcome, the more so since the larger terpene disintegration products such as bisabolene (Part I) and dihydro-ψ-ionone (preceding paper) were only isolated in very small amount, and consequently their formation is open to possible criticism. It has become abundantly clear that, if further insight is to be gained into the structure of the hydrocarbon, it is necessary in the first instance to render the molecule less liable to complete disruption under the action of oxidising agents. In order to accomplish this, we have now hydrogenated squalene to a point where five of the six ethenoid linkages would theoretically be saturated and then treated the product with ozone. After decomposition with water and removal of peroxides (see experimental), the oxidation products were separated into acid and neutral components. The examination of these has confirmed the work described in Part II of this series (Heilbron, Hilditch, and Kamm, J., 1926, 3131) and proves beyond doubt that the hydrogenation process is not only largely selective but leads to the formation of isomeric decahydrosqualenes. Dodecahydrosqualene (squalane) is also present to the extent of approximately 25%, from which it follows that products hydrogenated to a lesser degree than the decahydrosqualene must also have been formed.

Neutral Products.—(*a*) *Steam-volatile.* When the whole of the neutral oil was subjected to a short steam distillation, a readily volatile, pleasant-smelling liquid passed over. This was extracted

with ether and on fractionation gave as principal fraction a colourless liquid, b. p. 164—166°/765 mm., which we have characterised as *methyl isohexyl ketone*, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe$.

(b) *Non-steam-volatile.* The residue from the steam distillation was collected and separated by distillation under reduced pressure into large primary fractions. Each of these was refractionated and, after suitable distillates had been united, a further fractionation gave the following: (A) b. p. 125—145°/12 mm., (B) 155—175°/3 mm., (C) 200—210°/2 mm.

Fraction A. Further distillation of the fraction yielded a pale yellow liquid, b. p. 119—121°/11 mm. (semicarbazone, m. p. 97—98°), which has been definitely identified as hexahydro-ψ-ionone, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot COMe$.

Fraction B. After repeated distillation, a definite ketone fraction was obtained, b. p. 136—139°/1·5 mm., $n_D^{20°}$ 1·4461. In view of the isolation of methyl *iso*hexyl ketone and hexahydro-ψ-ionone, it was thought that the product would most likely be the next isoprene homologue, 2 : 6 : 10-trimethyl-14-pentadecanone,

$$CHMe_2\cdot[CH_2]_3\cdot[CHMe(CH_2)_3]_2\cdot COMe.$$

This ketone was accordingly synthesised from farnesol and isolated as a colourless liquid, b. p. 143°/3 mm., $n_D^{20°}$ 1·4435.* The semicarbazones of both ketones were prepared: that from the squalene product melted at 71·5—73·5°; the synthetic semicarbazone melted definitely lower (70—70·5°), but showed no depression when mixed with the former. Despite this fact, results based upon repeated ultimate analyses of the two semicarbazones prove conclusively that they are not identical and that the squalene ketone has the higher molecular formula $C_{19}H_{38}O$.

Fraction C. Analysis of this fraction indicated that it consisted of a mixture of squalane and some oxygen-containing substance, the character of which was shown by its removal by means of sodium bisulphite solution. The regenerated ketone, after distillation in a vacuum, gave analytical results agreeing with the formula $C_{23}H_{46}O$ or $C_{24}H_{48}O$.

Intermediate fractions. The various fractions with boiling points intermediate between those already recorded were each treated with semicarbazide acetate, and the solids formed submitted to very careful fractional crystallisation, without, however, revealing the presence of any semicarbazone other than those already described.

* After this synthesis was completed, an account of this ketone was published by F. G. Fischer (*Annalen*, 1928, **464**, 69). This author gives the melting point of the semicarbazone as 66—67°. The higher melting point recorded by us was only reached by working with comparatively large quantities and after numerous crystallisations.

Acid Products.—The acid products were converted into their methyl esters and roughly separated by fractional distillation into three distinct fractions and a very high-boiling residue which has not been examined in detail. The lowest-boiling fraction upon redistillation yielded mainly a colourless liquid, b. p. 139—141°/750 mm. The regenerated acid, which gave a solid anilide, m. p. 111—112°, was identified as γ-methyl-*n*-valeric acid.

The second main distillate, after further fractionation, was obtained as a colourless liquid, b. p. 105—107°/13 mm., which yielded an amide, m. p. 80—81°. Analytical values for both the ester and the amide pointed to their being derived from an acid $C_{11}H_{22}O_2$. In view of the isolation of γ-methyl-*n*-valeric acid it seemed highly probable that this acid would be 4 : 8-*dimethylnonoic acid*, and this surmise was confirmed by the synthesis of the acid from hexahydro-ψ-ionone by oxidation with chromic acid.

The final definite ester fraction consisted of a pale yellow liquid, b. p. 145—148°/5 mm. As attempts to prepare solid derivatives of the corresponding acid failed, this was carefully fractionated from a Willstätter bulb. The most abundant fraction boiled at 187—192°/2 mm. and gave analytical values in excellent agreement with the formula $C_{17}H_{34}O_2$.

Discussion of Results.

It was pointed out in Part V that all the reactions of squalene could be adequately explained on the assumption that the hydrocarbon exists in the two isomeric forms (I) and (II).

(I.) (*c*) $CMe\cdot[CH_2]_2\cdot CH{:}CMe\cdot[CH_2]_2\cdot CH{:}CMe_2$ [the first C:C linkage is marked (*b*)]
$\quad\quad\quad\Vert$
$CH\cdot[CH_2]_2\cdot CMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CHMe$
←-------------------Acid $C_{17}H_{34}O_2$-------------------→

(II.) $CMe_2{:}CH\cdot CH_2\cdot[CH_2\cdot C({:}CH_2)\cdot CH_2\cdot CH_2]_4\cdot CH_2\cdot CMe{:}CHMe$

The results now obtained afford striking evidence of the correctness of formula (I). For instance, the isolation in good yield of methyl *iso*hexyl ketone and hexahydro-ψ-ionone conclusively establishes the presence of the ethenoid linkages (*b*) and (*c*). As regards the remaining portion of the molecule, it necessarily follows from the isolation of the latter ketone that an acid constituent having the molecular formula $C_{17}H_{34}O_2$ should also be present. The fact that such an acid has actually been obtained coincides too well with the theoretical requirements to be merely fortuitous, and there can be little doubt that, despite the lack of definite constitutional proof, this acid is 3 : 7 : 11-*trimethyltetradecoic acid*.

Turning now to the question of the mode of formation of γ-methyl-

n-valeric acid and 4 : 8-dimethylnonoic acid, it is obvious that these could not possibly be formed directly through fission at the double bond of any of the mono-olefins derived from (I). It is also certain that they have not originated through further oxidation of any of the ketones primarily produced, as the conditions employed in the decomposition of the ozonides wholly preclude this possibility, *i.e.*, 4 : 8-dimethylnonoic acid could not have arisen from secondary oxidation of hexahydro-ψ-ionone but must have resulted from cleavage of the molecule at an ethenoid linkage *already present* in the hydrocarbon. As regards formula (II), it is practically certain, as pointed out in Part II, that the CH_2:C< groups would be the primary points for hydrogen addition, in which case ozonisation of the resultant decahydrosqualene could only give rise to an acid of very high molecular weight ($C_{27}H_{54}O_2$). We are thus forced to conclude that squalene exists in still another stable form, the structure of which must correspond to formula (III).

←------------ $C_{11}H_{22}O_2$ acid ------------→

(III.) (*e*) CH·$[CH_2]_2$·CMe:(*d*)CH·CH_2·CH:CMe_2
‖
CMe·$[CH_2]_2$·CH:CMe·$[CH_2]_2$·CH:CMe·$[CH_2]_3$·CMe:CHMe

←------------------------ $C_{19}H_{38}O$ ketone ------------------------→

Additional evidence of the existence of this isomeride is supplie through the isolation of the $C_{19}H_{38}O$ ketone which, like the above mentioned acids, cannot be accommodated by formula (I) or (II) Although its structure has not been directly elucidated, its strikin similarity to 2 : 6 : 10-trimethyl-14-pentadecanone suggests a closel analogous structure. This fact, taken in conjunction with th formation of 4 : 8-dimethylnonoic acid, leads to the conclusion tha the ketone is *3 : 7 : 11-trimethyl-15-hexadecanone* and that it ha originated through scission of a decahydrosqualene at the ethenoi linkage (*e*) (formula III). The production of γ-methyl-*n*-valeri acid similarly demands the presence of *3 : 7 : 11 : 15-tetramethy 19-eicosanone* (scission at *d*), and there is no reason to doubt th the high-boiling ketone separated from dodecahydrosqualene actually this substance.

Finally, a review of the ketones and acids produced leads to th conclusion that the addition of hydrogen proceeds from that pa of the molecule already containing the two hydrogen atoms add tional to the simple triterpene formula, *i.e.*, from the termin group CMe:CHMe common to all three isomeric forms. Th assumption is necessary in order to explain the absence of a ketone (*i.e.*, 2 : 6 : 10-trimethyl-14-pentadecanone) of higher mol cular weight than hexahydro-ψ-ionone from the hydrogenat

products from (I) or of fatty acid more complex than 4 : 8-dimethylnonoic acid from (III).

EXPERIMENTAL.

Preparation of the Ozonide.—Squalene obtained by the distillation method from the liver oil of *Centrophorus granulosus* (Heilbron, Kamm, and Owens, J., 1926, 1638) was treated with hydrogen in the presence of nickel catalyst until an absorption of 5 mols. of hydrogen had occurred (compare Heilbron, Hilditch, and Kamm, *loc. cit.*). The crude product was twice distilled, the final distillate boiling at 227—230°/3 mm. (Found : iodine value, 61. Calc. for $C_{30}H_{50}|^{=}_{1}$: iodine value, 62). This was then treated in chloroform solution (150 g. of hydrocarbon in 450 g. of solvent) at 0° with oxygen containing 5% of ozone, the gas being passed in at the rate of 10 litres per hour until a sample no longer absorbed bromine (30 hours). The chloroform was removed under reduced pressure first at the ordinary temperature and then at 100° for 30 minutes. The ozonide formed a clear, colourless, oily liquid lighter than water and possessing a pungent, clinging odour.

Decomposition of the Ozonide Mixture.—The ozonide was decomposed by boiling with water (300 c.c.) for 2 hours under reflux in an atmosphere of nitrogen, the gases evolved being passed successively through water and baryta solution; during the decomposition, a small amount of barium carbonate was deposited in the latter. The reaction mixture was acid to litmus, reduced Fehling's solution, and readily liberated iodine from potassium iodide solution, thus showing the presence of organic peroxides. These were decomposed by boiling the mixture with potassium hydroxide solution (75 c.c. of 50%) for 15 minutes, a treatment which simultaneously destroyed the aldehydes. Both the decomposition of the ozonide and the subsequent destruction of the peroxides proceeded smoothly. The reaction mixture was diluted with water and repeatedly extracted with ether. The alkaline portion was acidified with dilute sulphuric acid and the acids were removed by ether extraction and worked up as subsequently described. After removal of solvent from the neutral ethereal solution, the residue was subjected to distillation in steam, 2000 c.c. of distillate being collected. Both the distillate and the residue were saturated with sodium chloride and extracted with ether, and the ethereal solutions dried over anhydrous sodium sulphate. Under these conditions, 450 g. of hydrogenated squalene gave 502 g. of ozonide, from which 16 g. of steam-volatile ketone, 287 g. of neutral, non-steam-volatile matter, including about 35% of squalene, and 178 g. of mixed acids were obtained. The weight of barium carbonate collected

amounted to 3·1 g. The aqueous solution through which the gases and low-boiling volatile material had passed was examined for the presence of acetone and formaldehyde, but no trace of either could be detected.

Steam-volatile fraction. The bulk of this distilled at 164—166°/765 mm., forming a colourless, mobile liquid possessing a strong, carraway-like odour (Found : C, 74·7, 74·6; H, 12·7, 12·7. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%). It failed to reduce Fehling's solution but readily gave a crystalline addition compound with sodium bisulphite solution. The *semicarbazone*, which was prepared in the usual manner, formed almost immediately and, after three crystallisations from acetone, gave colourless, glistening plates, m. p. 149—150° (Found : C, 58·4, 58·3; H, 10·2, 10·4; N, 22·6. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3; N, 22·7%). These data agree well with the values for methyl *iso*hexyl ketone, which was synthesised by condensing *iso*amyl iodide with ethyl acetoacetate and hydrolysing the *iso*amylacetoacetic ester produced (compare Clarke, *J. Amer. Chem. Soc.*, 1909, **31**, 3). The ketone gave a semicarbazone, m. p. 152—153°, which showed no depression in melting point in admixture with the semicarbazone described above.

Non-volatile neutral portion. This was first roughly separated into the following fractions, leaving a residue of 18·4 g.

Fract.	Press. (mm.).	Temp.	Wt. (g.).	Fract.	Press. (mm.).	Temp.	Wt. (g.).
1	12·5	80—100°	9·8	4	3·0	170—200°	28·6
2	,,	100—150	17·9	5	,,	200—225	178·5
3	,,	150—200	17·6	6	2·0	225—245	11·3

Redistillation of fraction 1 yielded a further small quantity of methyl *iso*hexyl ketone and a higher-boiling fraction, which was combined with 2. Fraction 3 was similarly divided into a low- and a high-boiling portion, and the former also added to 2. Redistillation of these combined fractions provided a main distillate, b. p. 125—145°/12 mm. (14·5 g.).

Hexahydro-ψ-ionone.—On refractionation of the above, a main portion (5 g.) was collected as a slightly yellow liquid, b. p. 119—121°/11 mm., possessing a faint, clinging odour (Found : C, 78·2, 78·3; H, 13·2, 13·2. Calc. for $C_{12}H_{24}O$: C, 78·3; H, 13·0%. Calc. for $C_{13}H_{26}O$: C, 78·8; H, 13·1%). The ketone, which yielded a crystalline bisulphite addition product, was converted into its semicarbazone, which separated from methyl alcohol in colourless, glistening plates, m. p. 97—98° (Found : C, 65·7; H, 11·6; N, 16·5. Calc. for $C_{13}H_{27}ON_3$: C, 64·7; H, 11·2; N, 17·6%. Calc. for $C_{14}H_{29}ON_3$: C, 65·9; H, 11·4; N, 16·5%). The ketone was

regenerated by refluxing the semicarbazone with oxalic acid in aqueous-alcoholic solution and, after distillation, gave the following analytical values: C, 78·6, 78·5; H, 13·3, 13·3%, in excellent agreement with those required for $C_{13}H_{26}O$. Hexahydro-ψ-ionone was synthesised according to Ishizaka's method (*Ber.*, 1914, **47**, 2453), the only modification being that the hydrogenation of the geraniol was carried out at 130° under pressure, a nickel catalyst supported on charcoal being used in place of platinum-black. The semicarbazone obtained from the synthetic ketone melted at 97—98°, alone or mixed with the semicarbazone described above.

3 : 7 : 11-*Trimethyl*-15-*hexadecanone*.—Fraction 4 was combined with the residue of fraction 3 and distilled, giving as main fraction a portion (18 g.), b. p. 155—175°/3 mm. On further fractionation the ketone was obtained as a pale yellow, odourless, oily liquid (7·5 g.), b. p. 136—139°/1·5 mm. (Found: C, 80·3; H, 13·6. Calc. for $C_{18}H_{36}O$: C, 80·6; H, 13·5. Calc. for $C_{19}H_{38}O$: C, 80·9; H, 13·5%). The *semicarbazone* was prepared in the usual manner in methyl-alcoholic solution, a large volume of solvent being necessary in order to maintain the ketone in solution. After 7 days, the reaction mixture was poured into water, and the sticky solid collected and pressed on a porous tile. The semicarbazone was purified with difficulty by repeated crystallisation, first by slow evaporation of a methyl-alcoholic solution, and finally from ice-cold methyl alcohol (ice-jacketed filter). It formed colourless plates, m. p. 71·5—73·5° [Found: (micro), C, 71·2; H, 12·3; N, 12·3, 12·5. $C_{19}H_{39}ON_3$ requires C, 70·2; H, 12·0; N, 12·9%. $C_{20}H_{41}ON_3$ requires C, 70·8; H, 12·1; N, 12·4%].

3 : 7 : 11 : 15-*Tetramethyl*-19-*eicosanone* (?).—This ketone was contained in the high-boiling neutral fraction (146 g.), b. p. 200—210°/2 mm., obtained by refractionation of fraction 5. Analysis of this showed that it consisted of a mixture of squalane and some oxygen-containing substance (Found: C, 84·5; H, 14·6. Calc. for $C_{30}H_{62}$: C, 85·3; H, 14·7%). The oil was diluted with ether and shaken for 30 days with saturated sodium bisulphite solution, and the deposited solid separated by filtration and thoroughly washed with ether. The bisulphite product was decomposed with sodium carbonate solution, and the ketone, isolated by means of ether, was distilled, the main fraction being collected at 195—205°/3 mm. (Found: C, 81·5, 81·7; H, 13·5, 13·7. Calc. for $C_{23}H_{46}O$: C, 81·7; H, 13·6%. Calc. for $C_{24}H_{48}O$: C, 81·8; H, 13·6%).

Hexahydrofarnesol.—Farnesol (50 g.) was hydrogenated at 100° by means of nickel supported on charcoal (5 g. of catalyst containing 15% of nickel). After 2 hours, the absorption of the hydrogen had practically ceased and the mixture was accordingly cooled,

filtered, and treated with fresh catalyst (5 g.). When the temperature was now raised to 130°, the theoretical amount of hydrogen was absorbed in 30 minutes. The cooled filtered liquid was fractionated, practically the whole distilling at 125—128°/3 mm. It had $n_D^{18°}$ 1·4469, $d_4^{18°}$ 0·8361, whence $[R_L]_D = 72·9$ (Found: C, 78·6, 78·8; H, 14·2, 14·2. Calc. for $C_{15}H_{32}O$: C, 79·0; H, 14·0%; $[R_L]_D$, 72·7).

Hexahydrofarnesyl Bromide (12-bromo-2:6:10-trimethyldodecane).—This was prepared substantially as described by Fischer (*loc. cit.*). It formed a colourless, mobile liquid with a faint odour, b. p. 122°/4 mm., $n_D^{18°}$ 1·4605, $d_4^{18°}$ 1·001 (Found: Br, 27·4, 27·5. Calc. for $C_{15}H_{31}Br$: Br, 27·5%).

Hexahydrofarnesylacetoacetic ester formed a colourless liquid, b. p. 175—178°/3 mm., $n_D^{18°}$ 1·4484, $d_4^{18°}$ 0·9014 (Found: C, 74·3, 74·1; H, 12·0, 12·1. Calc. for $C_{21}H_{40}O_3$: C, 74·1; H, 11·4%).

2 : 6 : 10-*Trimethyl*-14-*pentadecanone*.—The preceding ester was decomposed by alcoholic potassium hydroxide solution at room temperature substantially as recorded by Fischer (*loc. cit.*). The ketone (10·5 g.) formed a colourless, odourless liquid, b. p. 142—143°/3 mm., $n_D^{19°}$ 1·4435, $d_4^{19°}$ 0·8403, whence $[R_L]_D = 84·6$ (Found: C, 80·6, 80·5; H, 13·3, 13·4. Calc. for $C_{18}H_{36}O$: C, 80·6; H, 13·5%; $[R_L]_D$, 85·1). The semicarbazone was obtained after many crystallisations from ice-cold methyl alcohol in colourless, glistening plates, m. p. 70—70·5° (Found: C, 70·3; H, 12·2; N, 12·9. Calc. for $C_{19}H_{39}ON_3$: C, 70·2; H, 12·0; N, 12·9%).

Acid Products.—The crude acid mixture was esterified by means of methyl alcohol and sulphuric acid, giving a brownish-yellow liquid (170 g.) with an odour reminiscent of *iso*butyric acid. The esters were separated by distillation at 15 mm. into the following fractions: (1) up to 110° (31 g.), (2) 110—150° (32 g.), (3) 150—200° (39 g.), (4) 200—245° (53 g.), residue (13 g.). Each was again distilled and, after suitable fractions had been united, a further series of distillations resulted in the formation of the following three portions: (a) 155—165°/756 mm. (5 g.), (b) 100—110°/13 mm. (17 g.), (c) 140—150°/5 mm. (17 g.).

γ-*Methyl*-n-*valeric Acid*.—Fraction (a) consisted of a colourless liquid which upon fractionation distilled almost wholly at 139—141°/750 mm. (3·9 g.) (Found: C, 64·4; H, 11·0; sap. equiv., 136. Calc. for $C_7H_{14}O_2$: C, 64·7; H, 10·8%; sap. equiv., 130). The ester was hydrolysed, and the acid converted into the anilide by refluxing with twice its weight of distilled aniline for 24 hours. The crude product was crystallised from aqueous alcohol in presence of animal charcoal, separating in long, colourless needles, m. p. 110—112° (Found: C, 75·3, 75·5; H, 9·1, 9·1; N, 7·6. Calc. for

$C_{12}H_{17}ON$: C, 75·4; H, 8·9; N, 7·3%). These data are in good agreement with those recorded for γ-methyl-*n*-valeric acid, which was synthesised from malonic ester and *iso*butyl iodide (compare Bentley and Perkin, J., 1898, **73**, 48) and converted into its anilide, m. p. 111—112°. A mixed m. p. détermination of the two anilides showed no depression.

4 : 8-*Dimethylnonoic Acid*.—Further distillation of fraction (b) gave as main fraction a colourless liquid, b. p. 105—108°/3 mm. (7·8 g.), having a more pleasant though fainter odour than the first fraction (Found: C, 71·2; H, 11·8; sap. equiv., 189. Calc. for $C_{11}H_{22}O_2$: C, 71·0; H, 11·8%; sap. equiv., 186. Calc. for $C_{12}H_{24}O_2$: C, 72·0; H, 12·0%; sap. equiv., 200). The ester was hydrolysed, and the acid further purified by conversion into its sparingly soluble calcium salt, whereupon a small quantity of a more soluble salt (probably the salt of a dicarboxylic acid) was removed; but it was uot further investigated. The regenerated acid was then distilled and analysed, figures in good agreement with the formula $C_{11}H_{22}O_2$ being obtained (Found: C, 70·6, 70·5; H, 11·9, 11·9%; equivalent, 182). This was confirmed by the preparation of the *amide* through the acid chloride in the following manner. A solution of the acid (2·5 g.) in a mixture of dry benzene (10 c.c.) and light petroleum (25 c.c.) was heated under reflux with thionyl chloride (5 g.) until the action was completed. The crude acid chloride, after removal of solvent and excess of reagent, was mixed with alcoholic ammonia, and the amide, which solidified on standing, was repeatedly crystallised from ether–light petroleum, yielding colourless plates, m. p. 80—81° (Found: C, 71·1, 71·2; H, 12·6, 12·5; N, 7·7. $C_{11}H_{23}ON$ requires C, 71·3; H, 12·4; N, 7·6%).

4 : 8-Dimetbylnonoic acid was synthesised by heating a solution of synthetio hexahydro-ψ-ionone (2·5 g.) in glacial acetic acid for 4 hours at 80° with a solution of chromic acid (5 g.) in the same solvent. This treatment yielded 0·8 g. of acid and 1·3 g. of unchanged ketone, which was again treated in the same manner. The acid was converted into its amide, m. p. 77—79° (Found: N, 8·0%), as described above. The compound was identical in all respects with the amide from the natural product and showed no depression of melting point in admixture.

3 : 7 : 11-*Trimethyltetradecoic Acid* (?).—Fraction (c) on redistillation gave mainly a yellowish oil, b. p. 145—148°/5 mm. (15 g.) (Found: C, 74·6; H, 12·6; sap. equiv., 236. Calc. for $C_{15}H_{30}O_2$: C, 74·4; H, 12·4%; sap. equiv., 242. Calc. for $C_{16}H_{32}O_2$: C, 75·0; H, 12·5%; sap. equiv., 256. Calc. for $C_{17}H_{34}O_2$: C, 75·4; H, 12·6%; sap. equiv., 270). The ester was hydrolysed and attempts were made to obtain a solid derivative without success.

As it seemed probable that some dicarboxylic acid might be present, fractional distillation of the acid itself was carried out and fractions were collected for every 5° rise of temperature. This fractionation showed that the acid was indeed a mixture. The two bulkiest fractions, (a) b. p. 182—187°/5 mm. (3·0 g.), and (b) 187—192°/5 mm. (4·5 g.), were analysed [Found: (a) C, 75·1; H, 12·5%; equivalent, 261. (b) C, 75·3; H, 12·8%; equivalent, 264]. These results show that the acid has the formula $C_{17}H_{34}O_2$, and, taken in conjunction with the isolation of hexahydro-ψ-ionone, lead almost inevitably to the conclusion that it is in effect *3 : 7 : 11-trimethyltetradecoic acid*. The low values for carbon and hydrogen given by the methyl ester are probably due to contamination with small quantities of the ester of a keto- or dicarboxylic acid, either of which would originate through oxidation of some of the lesser hydrogenated squalene products to which attention has already been drawn (p. 883).

4 : 8-*Dimethylnonaldehyde* (?).—In certain experiments the reaction mixture, after the decomposition of the ozonide with water, was worked up without removal of the peroxides. Under these conditions certain fractions of the neutral portion (boiling between methyl *iso*hexyl ketone and hexahydro-ψ-ionone), on being treated with semicarbazide acetate, yielded, in addition to methyl *iso*hexyl ketone semicarbazone, a small quantity of a more soluble *semicarbazone*, which crystallised from acetone in colourless plates, m. p. 115—116° (Found: C, 63·1; H, 11·0; N, 18·8. $C_{12}H_{25}ON_3$ requires C, 63·4; H, 11·0; N, 18·4%). Hydrolysis of the semicarbazone yielded a liquid which readily reduced Fehling's solution. These results lead to the conclusion that the substance is 4 : 8-dimethylnonaldehyde. Unfortunately the quantity of aldehyde regenerated was too small to allow of further work being carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, March 9th, 1929.*]

CXVI.—*Synthesis of an Isomeride of Thyroxine, and of Related Compounds.*

By CHARLES ROBERT HARINGTON and WILLIAM MCCARTNEY.

THE elucidation of the constitution of thyroxine (Harington, *Biochem. J.*, 1926, **20**, 293; Harington and Barger, *ibid.*, 1927, **21**, 169) affords an opportunity for the investigation of the effects of various groups on the physiological action of this compound. It has been found that thyronine (deiodothyroxine: compare

Harington, *Biochem. J.*, 1928, **22**, 1430, footnote) is devoid of physiological activity, whereas 3 : 5-di-iodothyronine exhibits the characteristic action of thyroxine but in a much lower degree (Gaddum, *J. Physiol.*, 1927, **64**, 246); the same applies to 3 : 5 : 3′ : 5′-tetrabromothyronine (Gaddum, unpublished observation). Attempts to prepare tetraiodo-derivatives of thyronine other than thyroxine itself having failed, attention was directed to the synthesis of ββ-*di*(3 : 5-*di-iodo*-4-*hydroxyphenyl*)-α-*aminopropionic acid*, $(OH{\cdot}C_6H_2I_2)_2CH{\cdot}CH(NH_2){\cdot}CO_2H$, a substance isomeric with thyroxine and retaining the characteristic *o*-di-iodophenolic group of the latter, but differing from it in that the benzene rings are linked through carbon instead of through oxygen.

Di(4-methoxyphenyl)methyl chloride was brought into reaction with ethyl potassiophthalimidomalonate, and the product hydrolysed with potassium hydroxide; the resulting acid, when heated, passed into the *anhydride* of α-*o*-carboxybenzamido-ββ-di(4-methoxyphenyl)propionic acid, $(OMe{\cdot}C_6H_4)_2CH{-}\underset{\cdot NH\cdot CO-C_6H_4}{CH{\cdot}CO{\cdot}O{\cdot}CO}$, which, on boiling with hydriodic acid and acetic anhydride, gave α-*amino*-ββ-*di*(4-*hydroxyphenyl*)*propionic acid*; this, with iodine and ammonia, yielded the desired isomeride of thyroxine.

Neither this compound, nor the amine derived from it by elimination of carbon dioxide, showed any trace of the type of physiological activity characteristic of thyroxine; further, the pressor effect of the amine, as also that of its iodine-free precursor, was negligible (Gaddum, private communication). Below are also described the synthesis of α-*amino*-ββ-*diphenylpropionic acid* by a method precisely similar to that outlined above, and the preparation of 3′ : 5′-*dibromo*-3 : 5-*di-iodothyronine*, a compound which might be expected to have a physiological effect intermediate between those of 3 : 5-di-iodothyronine and thyroxine.

EXPERIMENTAL.

Ethyl Di(4-*methoxyphenyl*)*methylphthalimidomalonate*.—Di(4-methoxyphenyl)methyl chloride (Straus and Dützmann, *J. pr. Chem.*, 1921, **103**, 47) (1 mol.), dissolved in dry xylene, and freshly prepared ethyl potassiophthalimidomalonate (1 mol.) were heated together at 145° for 4 hours with occasional shaking (compare Stephen and Weizmann, J., 1914, **105**, 1152). The cooled solution was shaken with water, and the precipitate filtered off and washed with cold dilute potassium hydroxide solution and water; a further amount was obtained by drying the xylene solution, removing the solvent under diminished pressure, and rubbing the residual syrup with a little alcohol. The ester formed colourless prisms, m. p.

106°, from alcohol; yield, 75% (Found : C, 67·7; H, 5·5; N, 2·4. $C_{30}H_{29}O_8N$ requires C, 67·8; H, 5·8; N, 2·6%).

Anhydride of α-o-Carboxybenzamido-ββ-di(4-methoxyphenyl)propionic Acid.—The above ester (29·5 g.) was moistened with alcohol and heated on the steam-bath for 1 hour, with frequent stirring, with a solution of potassium hydroxide (37 g.) in water (75 c.c.). The mixture was cooled, and the potassium salt filtered off, washed with alcohol, and dissolved in warm water. The solution, after cooling as far as possible without separation of the salt, was acidified by addition first of acetic and then of hydrochloric acid; the precipitated acid was collected, dried (crude yield, 22 g.), and, without further purification, heated at 180—200°/13 mm. for 1 hour. As decarboxylation proceeded, the material first became soft and then hardened again; a small amount of phthalic anhydride sublimed into the neck of the flask. The solid cake remaining was dissolved in the minimum boiling glacial acetic acid, and the hot solution slightly diluted with water; on cooling, the *anhydride* separated in colourless prisms. After two further crystallisations it had m. p. 209—210°; yield, 75% (Found : C, 69·4; H, 4·8; N, 2·9. $C_{25}H_{21}O_6N$ requires C, 69·4; H, 4·9; N, 3·1%).

α-Amino-ββ-di(4-hydroxyphenyl)propionic Acid.—The anhydride (1 part) was boiled for 2 hours under reflux with a mixture of constant-boiling hydriodic acid (5 parts) and acetic anhydride (5 parts); the solution was evaporated to dryness under diminished pressure, the evaporation being repeated after addition of water. The residue was dissolved in boiling water, the cooled solution filtered and extracted twice with ether, the aqueous layer made faintly alkaline with ammonia and evaporated to dryness under diminished pressure, and the residue dissolved in the minimum boiling alcohol. On standing in the cold, the *amino-acid* separated slowly; the crystals were recrystallised from water (charcoal); further crops were obtained by concentration of the mother-liquors. The compound forms fine colourless needles which soften at 190—200° and melt at 241° (decomp.). When pure, it is fairly readily soluble in water and sparingly soluble in alcohol. The air-dried substance always contains some water, but does not appear to form a definite hydrate; for analysis it was dried in a vacuum over sulphuric acid (Found : C, 65·7; H, 5·7; N, 5·0. $C_{15}H_{15}O_4N$ requires C, 65·9; H, 5·5; N, 5·1%).

ββ-Di(3 : 5-di-iodo-4-hydroxyphenyl)-α-aminopropionic Acid.—The above-described amino-acid was dissolved in the minimum amount of ammonia (*d* 0·880), and the ice-cold solution treated with the calculated amount of iodine in potassium iodide (2·54*N*), the rate of addition being slackened in the later stages. The solution was

evaporated to dryness under diminished pressure, and the residue collected, washed with dilute acetic acid, and dissolved in boiling dilute aqueous-alcoholic hydrochloric acid. This solution was boiled with charcoal, filtered, and treated with sodium acetate until it was no longer acid to Congo-red; immediate separation of the product ensued; after one similar recrystallisation it formed a colourless sphaero-crystalline powder, m. p. 218° (decomp.); yield, 60%. The *compound* is very sparingly soluble in water or alcohol; the acidic salts also are sparingly soluble in water, but readily soluble in dilute alcohol (Found: N, 1·8; I, 65·1. $C_{15}H_{11}O_4NI_4$ requires N, 1·8; I, 65·3%).

ββ-*Di*(4-*hydroxyphenyl*)*ethylamine*.—α-Amino-ββ-di(4-hydroxyphenyl)propionic acid was heated in portions of 0·5 g. in a sublimation apparatus at 290—315°/2 mm.; rapid decarboxylation occurred and a crust of the impure amine formed on the condenser. The *product* was collected, washed with boiling ethyl acetate, and crystallised from a large volume of hot water, from which it separated in colourless needles, m. p. 207—208°; yield, 55% (Found: C, 73·3; H, 6·6; N, 6·1. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6; N, 6·1%). The base is readily soluble in methyl and ethyl alcohol, but almost insoluble in other organic solvents. The hydrochloride, which is very soluble in water, was obtained by addition of ether to a solution of the base in saturated alcoholic hydrogen chloride; recrystallised from a small volume of alcohol, it had m. p. 275°. The *tribenzoyl* derivative crystallised from alcohol in clusters of fine needles, m. p. 200° (Found: N, 2·6. $C_{35}H_{27}O_5N$ requires N, 2·7%).

ββ-*Di*(3 : 5-*di-iodo*-4-*hydroxyphenyl*)*ethylamine*.—The above-described base (1 g.) was dissolved in ammonia solution (*d* 0·880; 150 c.c.) and the theoretical amount of iodine in potassium iodide (2·54*N*) was run in slowly, without cooling; the product began to separate after about half the iodine had been added. After standing for a few hours, the solution was diluted and the product collected. It was suspended in a large volume of dilute sulphuric acid, traces of free iodine were removed by addition of a little bisulphite, an equal volume of alcohol was added, and the solution heated to boiling and filtered. The filtrate was further diluted with water containing a little sulphuric acid, freed from alcohol by boiling, and again rapidly filtered to remove some tar. The final filtrate, on cooling, deposited the sulphate of the new base. The crystals were collected and dissolved in boiling 50% alcohol and the solution was treated with a slight excess of ammonia and concentrated by boiling until the *base* began to separate. The product was purified by re-solution in ammonia, followed by evaporation of the

excess of the latter; it then separated in clusters of colourless needles, m. p. 232—233° (decomp. with liberation of iodine); yield, 30% (Found: N, 1·9. $C_{14}H_{11}O_2NI_4$ requires N, 1·9%. The results of the iodine analyses of this compound were consistently about 1% low for a reason at present unexplained; there seemed to be no question as to its purity). The base is insoluble in water and alcohol and readily soluble in dilute aqueous sodium hydroxide and in dilute aqueous-alcoholic hydrochloric or sulphuric acid.

Ethyl Diphenylmethylphthalimidomalonate. — Diphenylmethyl bromide (Claisen, *Annalen*, 1925, **442**, 245, footnote) was condensed with ethyl potassiophthalimidomalonate precisely as described above for the corresponding *p*-dimethoxy-compound. The *product* remained in the xylene layer, when the xylene solution was mixed with water, and was obtained by drying the layer over calcium chloride, evaporating the xylene under diminished pressure, and crystallising the residue from a little alcohol; it formed colourless prisms, m. p. 117°; yield, 57% (Found: C, 70·9; H, 5·3; N, 3·0. $C_{28}H_{25}O_6N$ requires C, 71·3; H, 5·3; N, 3·0%).

Anhydride of α-o-Carboxybenzamido-ββ-diphenylpropionic Acid.— The crude acid, obtained by hydrolysis of the above ester with potassium hydroxide, when heated under diminished pressure at 180—200°, gave the *anhydride,* which formed colourless prisms, m. p. 214—215°, from acetic acid; yield, theoretical (Found: C, 74·2; H, 4·7; N, 3·8. $C_{23}H_{17}O_4N$ requires C, 74·4; H, 4·6; N, 3·8%).

α-Amino-ββ-diphenylpropionic Acid.—The anhydride was boiled for 2 hours with a mixture of equal volumes of constant-boiling hydriodic acid and acetic anhydride (10 parts). After evaporation to dryness under diminished pressure, the residue was dissolved in water and the solution neutralised with ammonia, whereupon immediate precipitation of the *amino-acid* took place. For purification it was dissolved in hot water with the aid of a little ammonia and the solution was neutralised with acetic acid; the amino-acid formed large colourless prisms, m. p. 236° (decomp.); yield, 77% (Found: C, 74·6; H, 6·3; N, 5·6. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%). The compound is sparingly soluble in water and alcohol.

ββ-Diphenylethylamine.—This compound, which had already been prepared (Lipp, *Annalen*, 1926, **449**, 24; Rupe and Gisiger, *Helv. Chim. Acta*, 1925, **8**, 340), was obtained in improved yield by heating ββ-diphenylalanine with diphenylamine (compare Johnson and Daschavsky, *J. Biol. Chem.*, 1924—1925, **62**, 725; Abderhalden and Gebelein, *Z. physiol. Chem.*, 1926, **152**, 125). ββ-Diphenyl-

alanine (2 g.), mixed with diphenylamine (40 g.), was heated in a metal-bath, the air being displaced from the reaction flask by a current of hydrogen which was afterwards led through a wash-bottle containing dilute sulphuric acid; the temperature of the bath was raised from 200° to 250° in the course of an hour, by which time decarboxylation was complete. The reaction mixture was cooled and dissolved in benzene, the latter being then extracted with the dilute sulphuric acid which had been employed in the wash-bottle. The acid extract was treated with excess of sodium hydroxide, the precipitated oil collected with ether (crude yield, 75%), and the base purified by distillation; it had b. p. 180°/15 mm., m. p. 39—40°. The hydrochloride had m. p. 259° and the picrate m. p. 216—217°. The chloroaurate and the chloroplatinate also coincided in properties with those described by the above-mentioned workers.

3' : 5'-*Dibromo*-3 : 5-*di-iodothyronine*.—3 : 5-Di-iodothyronine (0·53 g.) was suspended in glacial acetic acid (1·7 c.c.), and bromine (0·1 c.c.) in acetic acid (0·3 c.c.) added drop by drop; the addition was accompanied by evolution of heat and the amino-acid passed into solution. On keeping over-night in the ice-chest a crystalline precipitate separated; this was collected and dissolved in 50% alcoholic *N*-ammonium hydroxide. The ammoniacal solution was filtered, heated to boiling, and acidified with acetic acid; immediate crystallisation of the product ensued. The *compound* had m. p. 244·5° (decomp.); yield, 45% (Found: N, 2·1; I, 37·4. $C_{15}H_{11}O_4NBr_2I_2$ requires N, 2·1; I, 37·2%). In solubilities the substance closely resembled thyroxine.

DEPARTMENT OF PATHOLOGICAL CHEMISTRY, UNIVERSITY COLLEGE HOSPITAL MEDICAL SCHOOL, LONDON, AND DEPARTMENT OF MEDICAL CHEMISTRY, UNIVERSITY OF EDINBURGH.

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CXVII.—*Properties of Conjugated Compounds. Part VII. The Additive Formation of* cyclo*Hexenes.*

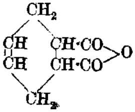
By ERNEST HAROLD FARMER and FRANK LOUIS WARREN.

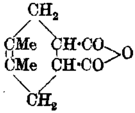
SEVERAL open-chain butadienes yield dimerides which are substituted *cyclo*hexenes; *cyclo*pentadiene and *cyclo*hexadiene yield polycyclic dimerides in which the additively formed rings are reputed (but not yet conclusively demonstrated) to be four-carbon and six-carbon structures respectively. If the opinions of Staudinger, Wieland, and their collaborators (*Helv. Chim. Acta*, 1924, 7, 23; *Annalen*, 1925, 446, 19) respecting the constitution of

di*cyclo*pentadiene be accepted, the *cyclo*hexene-forming tendency *cannot be regarded as an intrinsic property of the butadienès* (compare Lebedev's " butadiene type " of dimerisation, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249). The circumstances which determine the constitution of these and similar additive products are of the greatest interest in relation to butadienoid polarisation. The formation of both a *cyclo*butane and a *cyclo*hexene (corresponding to the formation of 1 : 2- and 1 : 4-dibromides) from the same hydrocarbon has never been reported and it remains to be discovered to what extent cyclic addition of the polymeric type is modifiable by varying the polar character, the spatial configuration or the length of the conjugated system of the hydrocarbon.

Recently Diels and Alder have published (*Annalen*, 1928, **460**, 98) an interpretation of the well-known reaction between *p*-benzoquinone and *cyclo*pentadiene and have extended the application of this addition to the combination of maleic anhydride, acraldehyde and similar reagents with butadienoid hydrocarbons in general. In so doing they have not only furnished an elegant method for the characterisation of conjugated hydrocarbons but have brought to notice a type of addition which is *outwardly* analogous to the polymeric process already mentioned. Since in these additions the difficulties which attend the control of purely polymeric processes and the recognition of the reaction products thereof are largely absent, the reagents of Diels and Alder are admirably suited to the study of additive behaviour. Employing, therefore, maleic anhydride as an addendum, we have made observations on the possibility of modifying the *cyclo*hexene-forming tendency.

Addition to Open-chain Butadienes.—Diels and Alder record that the simple open-chain and cyclic butadienes unite with maleic anhydride to give anhydro*cyclo*hexenes in quantitative yield. *All* the reaction products are assumed to be analogous to the compound (I) derived from butadiene itself, in which the presence of a six-carbon ring has been definitely established. We have confirmed the homogeneity of the products and the quantitative nature of the yields obtainable from the hydrocarbons examined by Diels and Alder and have found the same to hold with other hydrocarbons. Further, we have demonstrated that Diels and Alder's formula (I)


(I.)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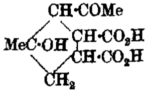
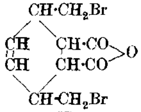

(III.)

(the position of the double bond had been assumed) is correct: the anhydride changes smoothly on oxidation into ββ′-dicarboxyadipic acid.

βγ-Dimethylbutadiene yields the *compound* (II), which is converted by ozonolysis into the ketonic acid

$$COMe{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}COMe,$$

or its cyclised equivalent (III). αζ-Dibromo-$\Delta^{\beta\delta}$-hexadiene yields (on heating with maleic anhydride) a crystalline derivative to which the formula (IV) is assigned. This very stable *anhydride containing* only one double bond (as determined by hydrogenation) yields almost quantitatively a *dilactone* (V), reducible catalytically to the saturated *lactone* (VI). The latter substance, however, could not be successfully oxidised to hexahydroprehnitic acid (VIII) for direct comparison with specimens obtained in the ways described below.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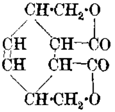
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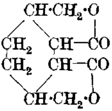
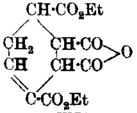

(VI.)

From these experiments and others carried out as a routine check on the purity of hydrocarbon samples, there is every reason to believe that *cyclo*hexene formation from open-chain butadienes is complete and remains unaffected (except as regards velocity of reaction) by variation of the position of the alkyl substituents.

Addition to Heterogeneous Conjugated Substances.—Ethyl muconate and sorbic acid react with maleic anhydride on prolonged heating. The additive product from the former gives oxalic acid so readily and extensively on treatment with permanganate or on ozonolysis that, in the absence of the observations of Baeyer (*Annalen*, 1890, **258**, 163) and Perkin and Pickles (J., 1905, **87**, 299) on the intense destructive action of permanganate on the hydrophthalic acids, its representation by a *cyclo*hexene structure such as (VII) would seem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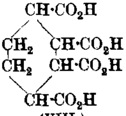
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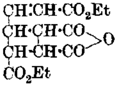
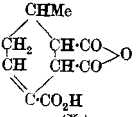

(IX.)

to be out of the question. It is converted, however, on reduction and hydrolysis into a stable tetrabasic *acid* which not only yields a

distillable *dianhydride* on treatment with acetyl chloride but shows no tendency, in the form of its *ester*, to undergo the Dieckmann reaction with sodium. These properties, although not absolutely identifying the reduced acid as hexahydroprehnitic acid (VIII), are inconsistent with the alternative formulation of the additive compound as the *cyclo*butane derivative (IX) or a Δ^{β}(etc.)-isomeride thereof. Complete proof has been sought by attempting to convert the *anhydro-ester* (VII) into the corresponding aromatic acid, prehnitic acid. Dehydrogenation, however, is not successful beyond the diolefinic stage, the final product being apparently a dihydroprehnitic acid. Ethyl *cis-cis*-muconate does not react appreciably with maleic anhydride even on prolonged heating.

The structure of the sorbic acid derivative is not easily demonstrable. The oxidation products are liquids, difficult to isolate in a pure state but of a character indicating their formation from the *cyclo*hexene compound (X) rather than from a corresponding *cyclo*butane compound. Since both additive products yield strongly enolic acids at an early stage during oxidation, $\alpha\beta$-positions are assigned to the double bonds in (VII) and (X).

Addition to Cyclic Butadienes.—The union of open-chain and cyclic butadienes with maleic anhydride is attended by the liberation of much heat; this is particularly striking with the cyclic hydrocarbons and reaches a maximum vigour with *cyclo*pentadiene. With *cyclo*hexadiene, the reaction appears to be a two-stage process in which the second stage, that of ring closure, is marked by the liberation of heat and is capable of acceleration or retardation, within limits, at will. The product is correctly represented by the *bridged cyclohexene* formula (XI), since it yields on oxidation the identical geometrical form of hexahydroprehnitic acid (VIII) previously derived from the muconic derivative (VII).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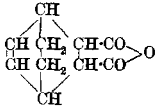
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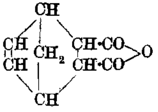
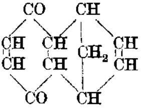

(XII.)

The correctness of Diels and Alder's formula (XII) for the *cyclo*pentadiene derivative is less certain, since it has not been possible to show that the tetracarboxylic acid derived by oxidation is unquestionably a *cyclo*pentane and not a *cyclo*butane derivative. On the contrary, although the anhydro-derivatives from *cyclo*pentadiene and *cyclo*hexadiene do not show any such difference in stability as that which characterises the hydrocarbon dimerides (one of these is

oxidised with ease and the other with great difficulty), the tetrabasic oxidation product of the former is definitely inferior in stability to all the *cyclo*hexane acids which have been examined and therefore may not safely be assumed to contain a *cyclo*pentane ring. Subsequent to the completion of this portion of our work, Diels and Alder's formula (XII) was attacked by Bergel and Widmann (*Annalen*, 1928, **467**, 76) on grounds of the correspondence in instability of the *cyclo*pentadiene-quinone compound (XIII) and di*cyclo*pentadiene. Since Bergel and Widmann have obtained by oxidation of the latter a liquid tetrabasic acid considered to be (XIV), it is suggested that the constitution of the maleic anhydride and quinone derivatives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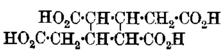
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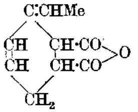
(XV.)

may well be analogous to that of di*cyclo*pentadiene, *i.e.*, contain an additively formed *cyclo*butane ring. The liquid tetrabasic acid now described by Bergel and Widmann was examined by one of us a year ago: its stability appears inferior to that to be expected of a *cyclo*pentane ring. Thus, although there are grounds for suspecting that *cyclo*pentadiene differs from other hydrocarbons in its mode of adding a non-dividing addendum, the definite production of *cyclo*butane forms is hardly to be considered as established beyond all doubt.

Addition to the $\Delta^{\alpha\gamma\epsilon}$*-Hexatrienes.*—Maleic anhydride may be added with ease to van Romburgh's hexatriene (*trans*), the reaction yielding almost quantitatively a crystalline anhydride: to this the constitution (XV) is assigned on the following grounds. Degradation by ozonolysis yields acetaldehyde and a very strongly enolic aldehyde the latter breaks down progressively on treatment with permanganate, apparently owing to the successive formation and decomposition of ketosuccinic (hydroxymaleic) acids, to yield oxalic acid as the main product [$CHO{\cdot}CO{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CHO \longrightarrow (CO_2H)_2 + HO_2C{\cdot}CO{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, etc.]. A similar decomposition takes place when the acid corresponding to (XV) is directly oxidised with permanganate.

cis-Hexatriene also combines additively with maleic anhydride The addition product appeared at first to be isomeric, rather than identical, with that from the *trans*-hydrocarbon. It was a slightly impure liquid which solidified only after numerous distillations and the lapse of many weeks; this behaviour was in strong contrast

with the remarkable crystallising capacity of the other anhydride. However, since from the first both anhydrides gave identical anilic acids and hydration products (as well as similar oxidation products), it is probable that the crystallisation of the newly obtained anhydride had merely been inhibited by impurity. This is the more likely in that any initial configurational difference between the products, due to the geometrical forms of the hydrocarbons, might be expected to disappear during the double-bond migration (presumably post-additive) which results in the appearance of ethylidene- instead of vinyl-*cyclo*hexenes.

trans-Hexatriene adds bromine both at the 1 : 2- and at the 1 : 6-positions (hitherto quinoline perbromide has been employed in preparing the 1 : 2-dibromide) : attachment at the 1 : 4-positions appears to be unfavoured. With maleic anhydride, there is exclusive attachment at the 1 : 4-carbon atoms, and the selection of the second point of attachment (at one or other of the even carbon atoms of the chain) seems not unconnected with the universal strong tendency towards the formation of six-carbon rings. Indeed it seems probable that, in all ring-forming additions of the type here considered, the intermolecular attachments are established consecutively and that the mode of completion of addition is determined—so far as choice between rival polarised centres of the butadiene chain is concerned—by configurational opportunism.

EXPERIMENTAL.

General Method.—The reactants in molecular proportion were kept in dry benzene solution. In some instances heating at 100° was necessary to effect addition (compare Diels and Alder, *loc. cit.*).

4 : 5-*Dimethyl*-cis-Δ^4-*tetrahydrophthalic anhydride* (II) was obtained quantitatively by keeping the solution of $\beta\gamma$-dimethylbutadiene and maleic anhydride for 24 hours at room temperature. It crystallised from petroleum (b. p. 60—80°) in long colourless needles, m. p. 78° (Found : C, 66·55; H, 6·65. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7%). When heated for a few minutes with ten times its weight of water, the anhydride yielded 4 : 5-*dimethyl*-cis-Δ^4-*tetrahydrophthalic acid*, which readily separated from the aqueous liquor and crystallised from aqueous alcohol in colourless prisms, m. p. 180—192° (Found : C, 60·6; H, 7·1; *M*, dibasic, 199. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; *M*, 198). The acid reverted partly to the anhydride at its melting point.

When a chloroform solution of the anhydride was ozonised for several hours, a solid, somewhat sticky ozonide separated. This, after removal of chloroform at room temperature, was kept with water for several weeks. The crystalline acid produced, much of

which could be filtered off directly and the remainder obtained by evaporating the aqueous liquor to dryness, was washed with ether and recrystallised from a small amount of water; m. p. 186°, with anhydride formation (Found : C, 51·9; H, 6·0; *M*, dibasic, 232. $C_{10}H_{14}O_6$ requires C, 52·15; H, 6·1%; *M*, 230). Of the two possible structures for this acid, octane-βη-dione-δε-dicarboxylic acid and the corresponding cyclol, *3-acetyl-4-methyl-*cyclo*pentan-4-ol-1 : 2-dicarboxylic acid* (III), the latter is regarded as correct; although the acid yielded crystalline derivatives with the usual reagents for ketones, it did not yield ββ'-dicarboxyadipic acid on further oxidation with permanganate or hypobromite.

An acid, which appears to be a lactonised form of the open-chain octanedionedicarboxylic acid, was precipitated when the original anhydride was heated for a few minutes with dilute nitric acid (1 : 1) and the solution cooled: it formed colourless flakes, m. p. 219°, softening at 210° [Found : *M* (monobasic), 232; *M* (dibasic towards hot baryta), 232].

cis-Δ^4-Tetrahydrophthalic anhydride was obtained quantitatively from butadiene and maleic anhydride by keeping the solution of the reactants for 24 hours. The melting points of the anhydride and of the corresponding *cis*-Δ^4-tetrahydrophthalic acid were identical with those recorded by Diels and Alder.

The anhydride (3 g.) was hydrolysed by warming with a slight excess of sodium bicarbonate solution, and the product oxidised at 0° with 3% permanganate solution in the usual way. The equivalent of 2 atoms of oxygen per molecule of anhydride was readily absorbed and a second 2 atoms more slowly. From the product, worked up in the usual way, ether extracted a slightly gummy crystalline acid, and a further quantity of the same acid was obtained by evaporating the aqueous mother-liquor to dryness and extracting the residue. This acid was the lower-melting stereo-form of βγ-dicarboxyadipic acid, a colourless crystalline powder, m. p. 188—189° (Found : C, 40·8; H, 4·3; *M*, tetrabasic, 236. Calc. : C, 41·0; H, 4·3%; *M*, 234). This form, in view of the spatial distribution in the parent isomeride, should represent the *meso*-isomeride: steric formulæ have not been allotted to the two dicarboxyadipic acids, but by analogy with αα'-dimethylsuccinic acid the lower-melting acid should have the *meso*-configuration.

*3 : 6-Dibromomethyl-*cis*-Δ^4-tetrahydrophthalic Anhydride* (IV).—Addition of maleic anhydride to αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene in benzene was effected at 100° during 5½ hours. The solvent was then removed from the almost black product, the residue mixed with dry ether, and the coarsely crystalline precipitate obtained recrystallised from light petroleum; it formed colourless slender needles

or (from benzene) short prisms, m. p. 98° (Found: Br, 47·4. $C_{10}H_{10}O_3Br_2$ requires Br, 47·3%). The ethereal liquor contained unchanged dibromide, maleic acid, and a further small quantity of the condensation product. Yield, 67%.

Careful oxidation of the *anhydride* with permanganate in neutral aqueous acetone, during which 4 atoms of oxygen per molecule were absorbed, yielded only gummy acids. The anhydride could not be hydrolysed by boiling water; when, however, it was boiled with aqueous sodium carbonate (2 mols. per mol. of anhydride), dissolution was slowly effected. The alkaline solution, after being boiled with charcoal and acidified, yielded white flakes, which recrystallised from water in fern-like leaves, m. p. 159—163° after softening at 147°. This substance, stable towards sodium bicarbonate, behaved as a *dilactone* (V) of 3 : 6-dihydroxymethyl-*cis*-Δ^4-tetrahydrophthalic acid (Found: C, 62·0; H, 5·1; *M*, dibasic, 196. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·15%; *M*, 194). Yield, 63%. Attempts to oxidise the sodium salt of the dihydroxy-acid to ββ'-dicarboxyadipic acid proved futile. Permanganate in particular caused extensive degradation to oxalic acid.

Lactone of 3 : 6-*Dihydroxymethylhexahydrophthalic Acid* (VI).—Catalytic reduction of the preceding lactone was readily effected, one molecule of hydrogen being absorbed. The saturated *lactone* crystallised from aqueous alcohol in colourless prisms, m. p. 119—120° (Found: C, 61·5; H, 6·1. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%). Attempts were made to oxidise this substance to hexahydroprehnitic acid by Fournier's method (*Bull. Soc. chim.*, 1909, 5, 920): the product was a mixture of oxalic acid and an acid (colourless prisms from water; m. p. 135°) which, although greatly resembling the acid sought, had approximately the composition $C_{10}H_{12}O_5$.

Addition to trans-αβ-*Dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene*.—A benzene solution of maleic anhydride and the dibromide (the latter prepared by the method of Farmer, Laroia, Switz, and Thorpe, J., 1927, 2953) in equimolecular proportion was kept for 12 hours and then heated for 5 hours at 100°. On removal of the solvent, a dark viscous mass remained from which no portion of the reactants could be recovered. Although addition had occurred, a pure addition product could not be isolated. Isomerisation of the αβ-dibromide had occurred to some extent during the heating, since a quantity of the dilactone, m. p. 159—163°, derivable from αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene was obtained by boiling the crude condensation product with aqueous sodium carbonate for 20 minutes.

3 : 6-*Dicarbethoxy*-Δ^4-*tetrahydrophthalic anhydride* (VII) was prepared from maleic anhydride and ethyl *trans-trans*-muconate at

100° (yield : 29% after 5 hours; 50% after 18 hours). It separated from the cooled reaction mixture in spherical crystal aggregates which, after twice crystallising from chloroform, formed white flakes, m. p. 185—188° (Found : C, 56·5; H, 5·4. $C_{14}H_{16}O_7$ requires C, 56·8; H, 5·4%).

The anhydro-ester was boiled with water for 20 minutes, and the cooled solution neutralised with sodium carbonate. The product was oxidised : 3% permanganate solution equivalent to 4 atoms of oxygen was supplied, the bulk of which was reduced in 3½ hours at 0° and the remainder on standing over-night at room temperature. The product, freed from manganese, was boiled for 20 minutes to complete the hydrolysis of ester groups; it was then concentrated to small bulk, acidified, and extracted with ether. The extract yielded oxalic acid mixed with a relatively small proportion of acidic gum. The yield of oxalic acid was much too large to be correlated with the amount of oxygen supplied. Reduction of the proportion of permanganate employed led to the production of an enolic syrupy acid and oxalic acid. Since the enolic material was invariably produced at an early stage in the reaction, the double bond is assigned to the Δ^3-position.

In order to discover whether double-bond movement occurred during opening of the anhydride ring the anhydro-ester was ozonised. The ozonide on warming with water lost carbon dioxide and yielded a deep yellow solution: the latter, however, on further oxidation with alkaline hydrogen peroxide, yielded oxalic acid as the only recognisable product.

From the anhydro-ester the corresponding tetraethyl ester (colourless prisms, m. p. 75°) was obtained by the action of alcoholic hydrogen chloride. By alternate addition of bromine, and removal of hydrogen bromide with diethylamine or pyridine, it was sought to convert the ester successively into ethyl dihydroprehnitate and ethyl prehnitate. The final product, however, after two such series of operations (in the second series, bromine was absorbed only under strong illumination) yielded on hydrolysis an *acid* corresponding in composition to dihydroprehnitic acid (colourless prisms from water; m. p. 241° with decomp.) (Found : C, 47·2; H, 3·1. $C_{10}H_8O_8$ requires C, 47·0; H, 3·1%).

3 : 6-*Dicarboxyhexahydrophthalic Acid* (*Hexahydroprehnitic Acid*) (VIII).—Dicarbethoxy-Δ^3-tetrahydrophthalic acid was hydrogenated catalytically in the presence of colloidal palladium. For this purpose the above-described anhydro-ester was boiled for 30 minutes with water, and the product diluted with alcohol. Addition of 1 mol. of hydrogen was complete in a few hours; prolonged treatment with hydrogen caused no further absorption. The

reduction product was isolated in the usual way and immediately hydrolysed with boiling dilute hydrochloric acid. On concentration of the acid solution to small bulk, the saturated *acid* separated slowly in large rectangular prisms containing $1H_2O$. These were twice recrystallised from very small quantities of water, and then had m. p. about 168° (variable with the rate of heating owing to anhydride formation) (Found : C, 43·0; H, 5·1; *M*, tetrabasic, 281. $C_{10}H_{12}O_8,H_2O$ requires C, 43·2; H, 5·05%; *M*, 278).

The *tetraethyl* ester, formed by saturating an alcoholic solution of the acid with hydrogen chloride, was a colourless oil, b. p. 238°/15 mm. (Found : C, 58·1; H, 7·5. $C_{18}H_{28}O_8$ requires C, 58·1; H, 7·5%). It was recovered unchanged after treatment in toluene with pulverised sodium.

The *dianhydride* separated in well-formed prisms, m. p. 223—225°, when the acid was refluxed for several hours with pure acetyl chloride (Found : C, 53·5; H, 3·5. $C_{10}H_8O_6$ requires C, 53·5; H, 3·5%). It distilled unchanged, save for slight resinification, at greatly reduced pressure.

6-Carboxy-3-methyl-cis-Δ^5-tetrahydrophthalic anhydride (X) was obtained by heating a benzene solution of maleic anhydride and sorbic acid for 18—38 hours at 100° and immediately pouring off the hot liquor from the hard prismatic mass which had separated. The latter very sparingly soluble substance (m. p. 174°) was purified by treating it several times with boiling benzene and with ether. Yield : 57% in 18 hours; 80% in 36 hours. The anhydride could be dissolved in boiling water without appreciable hydrolysis; boiling for 1 hour with water yielded *6-carboxy-3-methyl-*cis*-Δ^5-tetrahydrophthalic acid*, which formed colourless prisms, m. p. 194° with anhydride formation (Found : C, 52·5; H, 5·2; *M*, tribasic, 231. $C_{10}H_{12}O_6$ requires C, 52·6; H, 5·3%; *M*, 228).

The anhydride yielded a semi-solid ozonide, insoluble in chloroform. Decomposition of the ozonide with water yielded no volatile aldehyde; the syrupy aldehydic material obtained was extensively broken down to oxalic acid by further gentle oxidation with permanganate. When the anhydride was carefully oxidised with alkaline permanganate (3 atoms of oxygen per molecule of anhydride), no oxalic acid was produced, but an enolic acid which lost carbon dioxide on heating and was further oxidisable by alkaline hydrogen peroxide or sodium hypochlorite to a viscous polybasic acid. Although oxidation followed a course generally consistent with the formula assigned, the acidic products could not be obtained sufficiently pure for identification.

The acid, when catalytically hydrogenated in the presence of palladium, absorbed 1 mol. of hydrogen and gave *6-carboxy-3-methyl-*

cis-hexahydrophthalic acid, which crystallised from water in glistening prisms containing $1H_2O$, m. p. 194—196° (Found: C, 48·5; H, 6·5. *M*, tribasic, 247. $C_{10}H_{16}O_7$ requires C, 48·4; H, 6·45%; *M*, 248).

Addition to Cyclic Butadienes.—The addition of maleic anhydride to *cyclo*hexadiene (compare Diels and Alder, *loc. cit.*) was effected in various solvents. When the reactants were mixed, the solution (especially in benzene) assumed a deep yellow colour; after a few minutes, the temperature began to rise rapidly and the colour gradually faded; if the solution was kept cool, the yellow colour could be preserved for many hours. In the absence of a solvent reaction was very vigorous, the temperature rising to 150° and above, but in certain solvents, such as ether, the reaction was greatly retarded. The addition to *cyclo*pentadiene took place very vigorously in all solvents and explosively in the absence of a solvent.

Oxidation of Dicyclo*octenedicarboxylic Acid* (*Ethane*-$^{1:2}\Pi^{1:4}$-Δ^5-cyclo*hexene* - 2 : 3 - *dicarboxylic Acid*).—Oxidation of the *cyclo*hexadiene addition product with alkaline permanganate (4 atoms of oxygen per molecule) at 0° yielded a solid tetrabasic *acid*, m. p. 168° (decomp.), which formed colourless prisms containing $1H_2O$ (Found: C, 43·15; H, 5·0; *M*, tetrabasic, 281·6. $C_{10}H_{14}O_9$ requires C, 43·2; H, 5·0%; *M*, 278), mixed with a syrupy acid which appeared to be an impure form of the solid acid. The latter gave the same dianhydride and was in all observed respects identical with the acid obtained by hydrogenating the ethyl muconate addition product described above.

Oxidation of the cyclo*Pentadiene–Maleic Anhydride Condensation Product.*—Permanganate oxidation in this instance differed from all similar oxidations of hydrocarbon–maleic anhydride products in the indefiniteness of the end point and in the resinification which occurred (with blackening of the solution) during concentration of the oxidation liquor. These points are characteristic of the corresponding oxidation of *dicyclo*pentadiene. The dark brown viscous acid obtained deposited colourless prisms of a tetrabasic *acid*, m. p. 181—182° with anhydride formation (Found: C, 42·9; H, 4·2; *M*, tetrabasic, 250. $C_9H_{10}O_8$ requires C, 42·9; H, 4·1%; *M*, 246). Esterification of the non-solidifiable portion (*tetraethyl* ester, colourless mobile liquid, b. p. 226°/14 mm. Found: C, 57·0; H, 7·2. $C_{10}H_{16}O_8$ requires C, 57·0; H, 7·3%), followed by hydrolysis with hydrochloric acid, permitted separation of the resinous matter and the accumulation of considerable quantities of the solid acid. The attempts which have been made to determine whether this acid is to be regarded as *cyclo*pentane-1 : 2 : 3 : 4-tetracarboxylic acid or as *cyclo*butane-1 : 2 : 3-tricarboxy-4-acetic acid have so far been

without success. Unlike the analogous *cyclo*hexane acids, it gradually reduced alkaline permanganate.

Addition to trans-*Hexatriene*.—The benzene solution of maleic anhydride and hexatriene was kept at room temperature for 14 hours and then heated at 100° for 5 hours. After removal of the solvent at reduced pressure an oil remained which soon solidified (m. p. 46°). This substance, 3-*ethylidene*-cis-Δ^4-*tetrahydrophthalic anhydride*, separated from petroleum (b. p. 40—60°) in very long, colourless needles, m. p. 51·5°, b. p. 148°/6 mm. (Found: C, 67·6; H, 5·6. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). With aniline it yielded an *anilic acid* (colourless flakes, m. p. 174°. Found: C, 71·1; H, 6·2. $C_{16}H_{17}O_3N$ requires C, 70·85; H, 6·3%). Yield, quantitative.

On boiling with water for 10 minutes the anhydride passed into solution. Extraction of the cooled product with ether yielded the corresponding 3-*ethylidene*-cis-Δ^4-*tetrahydrophthalic acid*, which crystallised from water in colourless prisms, m. p. 164—166° with evolution of steam (Found: C, 61·4; H, 6·3; *M*, dibasic, 197·6. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%; *M*, 196).

Ozonisation of a chloroform solution of the anhydride at 0° for 9 hours caused the separation of a sticky ozonide which, after removal of the solvent, was gently heated with water. The vapours evolved during heating, smelling strongly of acetaldehyde, were swept by a stream of carbon dioxide into an acetic acid solution of β-naphthol containing some hydrochloric acid (compare Mulliken, "Identification of Pure Organic Compounds," I, 23). A considerable quantity of ethylidene-β-dinaphthyl oxide, m. p. 172·5° (mixed m. p. with authentic specimen, 172·5°), was obtained. The colourless aqueous liquor, which gave a very intense purple colour with ferric chloride, assumed a dark brown colour on boiling; on extraction with ether it yielded syrupy products from which only oxalic acid could be obtained on further oxidation with permanganate; on neutralisation with alkali and addition of ammonia it yielded a small amount (too small for investigation) of an insoluble calcium salt which had the characteristic properties of precipitated calcium tricarballylate.

The oxidation of the anhydride with ice-cold permanganate solution was studied in some detail. Invariably 7 atoms of oxygen per molecule of anhydride were readily taken up, after which reduction of permanganate became very slow. Isolation of the oxidation product at this stage—a stage corresponding to the production of α-oxalyltricarballylic acid—yielded a strongly enolic acid (intense purple colour with ferric chloride). Further oxidation of the latter with permanganate could be slowly accomplished at room temperature: interruption of the oxidation process and isolation of

the product from portions of the material yielded always oxalic acid and syrupy enolic acids until finally practically the whole of the original anhydride had been converted into oxalic acid.

Addition to cis-*Hexatriene*.—A benzene solution of the hydrocarbon (which contained a little of the *trans*-isomeride) and maleic anhydride was kept for 12 hours and then heated at 100° for 5 hours. From the cooled product, some insoluble matter (highly polymerised material) was filtered off, and the solvent removed at reduced pressure. The crude liquid anhydride obtained (yield, 83%; b. p. 120—150° after a very small proportion of maleic anhydride had distilled) was rigorously fractionated and specimens were analysed. All fractions were very slightly impure, although all gave nearly quantitative yields of an anilic acid and of an ethylidene-*cis*-tetrahydrophthalic acid identical with the corresponding compounds from the *trans*-hydrocarbon. Ultimately, after many distillations and the lapse of several weeks, practically the whole of the material solidified; the solid after two recrystallisations was found to be identical with the ethylidene-*cis*-tetrahydrophthalic anhydride derived from the *trans*-hydrocarbon. On ozonisation the once-distilled crude liquid anhydride gave results identical with those recorded for the pure solid anhydride.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CXVIII.—*The Oxidation of* d-Δ^4-*Carene with Beckmann's Chromic Acid Mixture.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

FOR the identification of d-Δ^4-carene in essential oils the only satisfactory method at present available consists in the oxidation of the appropriate fraction of the oil with potassium permanganate in acetone solution; d-1 : 1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid is then obtained, which can be characterised by the preparation of the semicarbazone, m. p. 182—183° (J., 1922, **121**, 2295). Although this method enabled Semmler and von Schiller (*Ber*., 1927, **60**, 1591) to establish the presence of the hydrocarbon in various oils and so confirm the conclusion previously reached by Rao and Simonsen (J., 1925, **127**, 2494) that sylvestrene does not occur in nature, it has the inherent defect that, unless great care is taken to remove all traces of α-pinene, the keto-acid is liable to be

contaminated with pinonic acid, which would render difficult the purification of the semicarbazone.

d-Δ^4-Carene, on oxidation with Beckmann's chromic acid mixture (compare this vol., p. 305), behaves in a similar manner to the Δ^3-isomeride. As the quantity of the terpene available for oxidation was limited, a complete investigation of the products formed in the reaction was not possible, but *l*-*trans*-caronic acid was isolated in excellent yield and it had the same m. p. and rotatory power as that described previously. The fact that the rotatory power was identical with that of the acid obtained from *d*-Δ^3-carene is of particular interest and enhances the desirability of the resolution of *dl*-*trans*-caronic acid into its optical enantiomorphs being undertaken.

EXPERIMENTAL.

The oxidation of the hydrocarbon, which had been separated from the oil from *Andropogon Jwarancusa* and carefully purified by distillation over sodium, was carried out under the conditions given previously (*loc. cit.*, p. 398) and proceeded much more rapidly and completely than in the case of *d*-Δ^3-carene. The *l*-*trans*-caronic acid obtained (3 g. from 50 c.c. of the terpene), after crystallising from water, had m. p. 202—203° (Found: C, 53·2; H, 6·7. Calc.: C, 53·2; H, 6·3%). The rotatory power was determined in alcoholic solution at 20°: $c = 2{\cdot}215$, $l = 4$, $\alpha_{5461} = -1{\cdot}05°$, whence $[\alpha]_{5461} = -11{\cdot}85°$. The identity of the acid was confirmed by its conversion into *cis*-caronic acid in the usual manner. From the original aqueous filtrate, by extraction with ether, a further quantity of *l*-*trans*-caronic acid (1·8 g.) was separated, and in addition terebic acid, m. p. 173—174° (alone and in admixture with an authentic specimen) and dimethylmalonic acid, decomp. 185—186° (Found: *M*, 138·8. Calc.: *M*, 138), were isolated.

A neutral oil, yielding a semicarbazone, m. p. 205—207°, was obtained, but the quantity was insufficient for analysis and identification.

GUY'S HOSPITAL MEDICAL SCHOOL,
(UNIVERSITY OF LONDON), S.E. 1. [*Received, March 19th*, 1929.]

CXIX.—*The Binary System Carbamide–Ammonium Nitrate. Molecular Association in each Component.*

By WILLIAM JOHN HOWELLS.

CARBAMIDE is known to form compounds with certain nitrates, *e.g.*, silver and mercuric, and one of the objects of this research was to determine whether it combined with ammonium nitrate. Also,

attempts are described to determine (*a*) the molecular depression of the freezing point for carbamide and for ammonium nitrate, and (*b*) the state of molecular association of certain compounds when dissolved in these two substances in the molten state.

EXPERIMENTAL.

The materials used were of a high degree of purity, and were powdered and dried carefully—generally in a water-oven, and for several days in the case of ammonium nitrate—before use. When not in use, they were kept over fused calcium chloride in a desiccator.

The freezing-point apparatus was of the usual kind. The outer jacket, a cylindrical glass jar, was wrapped in cotton-wool at the bottom, and the inner tube was a hard-glass test-tube (6″ × 1″) provided with a tightly fitting cork which carried a solid glass stirrer and two thermometers, one of which (a standard) dipped into the melt. The other thermometer, together with a third, outside the apparatus, enabled the correction for exposed stem to be made in two parts.

About 30 g. of pure dry ammonium nitrate were weighed into the hard-glass test-tube, which was tightly corked and heated in an oil-bath; as soon as the nitrate had melted, the tube was refitted with the thermometers and stirrer, left in the bath for a minute, then wiped and quickly placed in its jacket. The molten nitrate was stirred until crystals appeared throughout its bulk, whereupon the temperature rose slightly but rapidly to a stationary maximum, which was taken as the freezing point. The temperatures on both auxiliary thermometers were read immediately. In all cases, the mean of four such determinations was taken as the true freezing point.

A weighed quantity of carbamide was now introduced into the molten ammonium nitrate, and the freezing point redetermined. After two lots of carbamide had been added, a fresh quantity of nitrate was used. Subsequently, the freezing points were determined of pure carbamide and of its mixtures with weighed amounts of ammonium nitrate. The two molten liquids are miscible in all proportions. Very concentrated solutions exhibited no rise in temperature at their crystallisation point, so the temperature at which crystals appeared throughout the melt was taken as the freezing point; the reading was facilitated by placing a luminous flame behind the apparatus. With a few of the concentrated solutions, observations of a eutectic arrest were made.

As Saunders (J., 1922, **121**, 698) has shown that at 200° pure dry ammonium nitrate evolves 20 c.c. of gas per 50 g. per hour, the temperature in the present work was rarely taken above 180°: the

slight decomposition occurring, which was greater with mixtures, was negligible in all cases. The same is true for carbamide and its mixtures.

The results are in Table I, and are shown graphically in the figure.

TABLE I.

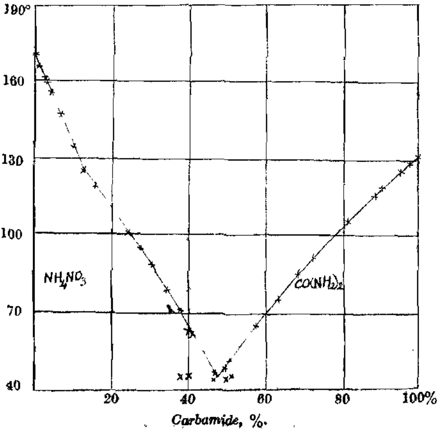
Freezing Points of Ammonium Nitrate and Carbamide Mixtures.

Carbamide, %.	F. p.	Carbamide, %.	F. p.	Carbamide, %.	F. p.	Carbamide, %.	F. p.
0	169·6°	15·08	120·8°	41·14	60·4°	80·24	106·2°
1·00	165·3	15·80	119·2	46·10	45·2 (*c*)	88·82	115·7
2·33	160·8	24·26	100·5	48·99	47·28(*d*)	90·1	118·1
2·65	159·7	27·36	93·9	49·95	51·0 (*e*)	95·56	125·65
3·47	156·7	29·90	87·9	57·5	65·2	95·61	126·1
5·87	148·3	33·90	77·9	63·6	76·0	97·93	129·0
9·77	135·5	37·30	71·3 (*a*)	68·07	85·2	98·83	130·2
12·19	126·0	40·00	61·38(*b*)	72·3	91·2	100·0	132·1

Eutectic arrests observed at points marked *a*, *b*, *c*, *d*, and *e* were at 45·1°, 44·45°, 44·85°, 44·05°, and 44·9°, respectively, the mean being 44·67°.

FIG. 1.

Ammonium nitrate + carbamide.



The freezing-point curve for the binary system consists of two limbs, giving a definite eutectic point, and there is no indication of the formation of a double compound. The eutectic point is at

44·7°, and the eutectic mixture contains 47% of carbamide, or 54·18 mols.%. This temperature is in close agreement with the mean of the eutectic arrests.

The left-hand limb of the curve shows a definite break at 126°, corresponding to the transition of the regular to the rhombohedral form of ammonium nitrate at 125°, but seems to pass smoothly through the transition point at 83°. It thus appears that the lower portion of this limb was obtained under metastable conditions.

Molecular Association in Ammonium Nitrate and in Carbamide.

The depression of the freezing point caused by the addition of dextrose, ammonium nitrate, and acetamide to carbamide (about 25 g.) was determined at three different concentrations in each case, and the corresponding molecular depressions were calculated; the results are in Table II (*a*), Δ being the observed depression.

TABLE II.

(*a*) Carbamide mixtures.

Substance added.	G. per 100 g. carbamide.	Δ.	Mol. depression.	*M*, calc.	*M*, obs.
$C_6H_{12}O_6$	2·024	2·42°	215	180	
	4·680	5·32	205	,,	
	6·450	7·20	201	,,	
NH_4NO_3	1·184	1·9	128	80	134
	2·114	3·1	117	,,	140
	2·880	4·0	111	,,	145
$CH_3{\cdot}CO{\cdot}NH_2$	0·800	1·07	79	59	161
	1·550	1·92	73	,,	166
	2·144	2·55	70	,,	169

(*b*) Ammonium nitrate mixtures.

Substance added.	G. per 100 g. NH_4NO_3.	Δ.	Mol. depression.	*M*, calc.	*M*, obs.
$CO(NH_2)_2$	2·386	8·8°	221	60	
,,	6·240	21·3	205	,,	
$CH_3{\cdot}CO{\cdot}NH_2$	2·362	8·22	205·3	59	63·5
,,	5·671	17·42	185	,,	65·4
$Ca(NO_3)_2$	2·060	3·34	266	164	141
[1] KNO_3	4·04	3·3	82·5	101	
,,	10·50	8·4	80·8	,,	
[2] H_2O	2·05	23·0	202	18	18·3
[3] $LiNO_3$	2·76	8·8	220	69	69
[4] $NaNO_3$	3·40	8·3	207·5	85	90·5
,,	8·84	20·0	192·3	,,	90·6
[5] NH_4Cl	5·60	12·9	123	53·5	89·2

[1] Perman and Howells, J., 1923, **123**, 2129.
[2] Millican, Joseph, and Lowry, J., 1922, **121**, 959.
[3] Perman and Harrison, J., 1924, **125**, 1709.
[4] Early and Lowry, J., 1922, **121**, 963.
[5] Perman, *ibid.*, p. 2473.

The figures obtained for dextrose at the concentrations indicated are in fair agreement with Blagden's law, but since the concordance is not exact, the values 215, 205, and 201 have, in turn, been adopted as the value of the molecular depression " constant " in deriving the calculated molecular weights at the three concentrations of the other two substances. The results show that ammonium nitrate and acetamide exhibit molecular association when dissolved in carbamide, and that their degrees of association increase slightly with increase in concentration, approaching the values 2 and 3 respectively at the concentrations involved. (Amides as a class show strong association in many solvents.)

Determinations of the freezing points were made when carbamide, acetamide, and calcium nitrate were added separately to about 30 g. of ammonium nitrate. (Dextrose was at once charred when added to the molten salt, and naphthalene, triphenylmethane, and diethylmalonylurea proved to be too sparingly soluble.) The results are in Table II (*b*), together with those for five other substances as calculated from published data.

The values of the molecular depressions for carbamide, lithium nitrate, and water are in close agreement, especially when they refer to approximately equal molecular concentrations; hence carbamide and lithium nitrate probably have their normal molecular weights, water being possibly slightly associated rather than dissociated. Consequently, 221 and 205 have been adopted as the values of the molecular depression " constants " for ammonium nitrate according as calculations are made at one or other of the two molecular concentrations concerned.

The figures in the last column indicate that acetamide is slightly associated, but not nearly to the same extent as when dissolved in molten carbamide. Sodium nitrate appears to be slightly associated. On the other hand, ammonium chloride is strongly associated in molten ammonium nitrate.

The molecular depression due to calcium nitrate, *viz.*, 266, was calculated from the depression of the freezing point caused by a concentration of 0·0126 mol. per 100 g. of ammonium nitrate. At this concentration carbamide produces a depression of 2·9° (value obtained from the curve) corresponding to a molecular depression of 229; hence, if carbamide is " normal " in ammonium nitrate solution, the observed molecular weight for calcium nitrate is 141, indicating some dissociation.

The abnormal results obtained with potassium nitrate are interesting, but the sub-normal molecular depression of the freezing point may be due, not only to molecular association of the solute (compare sodium nitrate, above), but also, at least in part, to the separation of

mixed crystals, which Perman and Howells (*J.*, 1923, **123**, 2128) have shown to exist.

It is intended to investigate the molecular depressions caused by the addition of rubidium, cæsium, and thallous nitrates to ammonium nitrate, since these metals and ammonium belong to a series of "isomorphous elements."

Summary.

1. The equilibrium curve for the binary system ammonium nitrate–carbamide consists of two limbs, and exhibits a eutectic point at 44·7° and 47% of carbamide. The ammonium nitrate exhibits a transition point at 126°. The two substances do not form a compound at the temperatures involved in these experiments.

2. For dilute solutions, the molecular depression per 100 g. of carbamide is approximately 215. Ammonium nitrate and acetamide are strongly associated in molten carbamide.

3. For dilute solutions in molten ammonium nitrate, the molecular depression is about 221 per 100 g. Carbamide, lithium nitrate, and water are all normal, or nearly so, in this solvent, but sodium nitrate and acetamide are slightly associated. Potassium nitrate causes a sub-normal depression of the freezing point, partly, at least, because it separates with the solvent in the form of mixed crystals. Calcium nitrate is slightly dissociated and ammonium chloride strongly associated in molten ammonium nitrate.

MUNICIPAL SECONDARY SCHOOL,
QUAKERS' YARD. [*Received, February 28th*, 1929.]

CXX.—*The Transformation of Phenylnitroamines into Nitroanilines. Part I.*

By ALAN EDWIN BRADFIELD and KENNEDY JOSEPH PREVITÉ ORTON.

THE isomeric change of aromatic nitroamines into nitroanilines, $Ar{\cdot}NH{\cdot}NO_2 \longrightarrow NO_2{\cdot}(Ar-H){\cdot}NH_2$, under the influence of mineral acids in aqueous or aqueous acetic acid media was first investigated in these laboratories some years ago, but only a preliminary account of the results has been published (Orton and Pearson, J., 1908, **93**, 725; Orton, Reed, and Thomas, *Brit. Assoc. Reps.*, 1912, 117; *Chem. News*, 1912, **106**, 236). The transformation of the nitroamines offers a striking contrast to the isomeric change of the chloroamines, in that all acids are effective catalysts of the former, whereas for the latter hydrochloric acid is essential (Orton, Soper, and Williams, J., 1928, 998). Moreover, the chlorination of one

anilide by the chloroamine of another [Ar·NClAc + Ar′·NHAc ⟶ Ar·NHAc + Cl·(Ar′–H)·NHAc] finds no complete and simple parallel in the interaction of a nitroamine with an anilide. Although indications have been obtained that it is sometimes possible for the nitro-group to migrate from a nitroamino-group of one substance and become attached to a carbon atom of another aniline or an anilide, no nitrating agent invariably and normally appears in the system in which a nitroamine is undergoing isomeric change, whereas the presence of chlorine can always be demonstrated during the isomeric change of a chloroamine. With the aid of more accurate modern apparatus, and with an extended range of material, the isomeric change of the nitroamines has again been examined by the authors.

Quantitative measurements of the rate of transformation of a nitroamine into the isomeric nitroaniline are most easily carried out when they are based on colorimetric estimates of the amount of nitroaniline appearing in the changing system, a method, however, which imposes severe limitations on the number of nitroamines which can be studied. Experience has shown that only nitroamines with one vacant ortho-position can be used, and that no source of colour other than the migrating nitro-group should be present.

The *nitroamines* derived *from* 2 : 4-dichloroaniline, 2 : 4-dibromoaniline, and 3-bromo-*p*-toluidine have been used, but the last-mentioned has considerable advantages over the others. The *measurements of the rate of isomerisation show that at least one* by-product is formed; a substance is always produced which is capable of coupling with a phenol to give an azo-compound. There are no *indications that this* by-product arises by *reduction* of the nitroamine by the acids or by the solvent. Purified acetic acid has no advantage over the commercial acid containing such impurities as formic acid; the proportion of by-products to nitroaniline and the rate of transformation are not appreciably different in the two media.

Under the conditions employed, with at least ten molecular proportions of the catalysing acid, nitroamine and by-product formation proceed as side reactions of the first order. No stoicheiometrical relation exists between the relative amounts of nitroaniline and by-products; the ratio varies with the concentration of the catalysing acid, the dilution of the acetic acid medium, and the nitroamine employed, but, in general, has the same value for different acids at equivalent concentrations. With sulphuric acid as catalyst, in 98% acetic acid, transformation of 3-*bromo*-p-*tolylnitroamine* proceeds at about one half the rate of transformation

with hydrochloric acid of the same normality : the effect of benzenesulphonic acid is intermediate. Dilution of the medium to 50% acetic acid causes a marked decrease in the velocity of the reaction. (See Table, where $k = k_1 + k_2 + \ldots$ the sum of the velocity coefficients for the separate side reactions.)

Transformation of 3-Bromo-p-tolylnitroamine.

Medium.	Acid as catalyst.	% Nitro-toluidine in product.	k.
98% Acetic acid	*0·02N-Hydrochloric acid*	*69*	*0·0110*
	0·1N- " "	73	0·0634
	1·0N- " "	76	very fast
	0·02N-Sulphuric acid	69	0·00501
	0·02N-Benzenesulphonic acid	69	0·00788
	0·1N-Nitric acid	*ca. 90*	*very slow*
50% Acetic acid	1·0N-Hydrochloric acid	81·5	0·00389
	1·0N-Nitric acid	81·5	0·00371

Transformation of 2 : 4-Dichlorophenylnitroamine in 98% Acetic Acid.

Acid as catalyst.	% Nitroaniline in product.	k.
0·1N-Hydrochloric acid	56	0·00238

The behaviour of nitric acid is abnormal. Although in 50% acetic acid nitric acid is a catalyst of approximately the same power as hydrochloric acid, in 98% acetic acid its action is very feeble, and by-product formation is almost absent. Some parallel to this is to be found in the anomalous catalytic behaviour of nitric acid in acetylation (Orton and Smith, J., 1908, **93**, 1242; 1909, **95**, 1060), the hydrolysis of acetic anhydride (Orton and M. Jones, J., 1912, **101**, 1708), and in the bromination of acetic anhydride (Orton, Watson, and Hughes, J., 1927, 2458). This result excludes the possibility of accounting for the transformation by a two-stage process, involving the production, by hydrolysis, of nitric acid, which then acts as the effective nitrating agent, unless the second stage, the nitration, is relatively very rapid. Direct experiment, however, shows that nitric acid (one mole/litre) in 50% *acetic acid effects in several days no appreciable substitution in* 3-bromo-*p*-toluidine.

As a whole the new experiments confirm in a satisfactory quantitative manner the results of the preliminary and less accurate work. The anion of the acid catalyst is not fundamentally concerned in the reaction, as it is in the isomeric change of the chloroamines, for which the presence of chloridion is essential. The facts are in harmony with the view that in the transformation of the nitroamines to nitroanilines an intramolecular process plays the important part. Nevertheless, unequivocal evidence has recently been

obtained that in certain circumstances extranuclear migration of the nitro-group to a foreign aniline nucleus can take place.

EXPERIMENTAL.

*Preparation of 3-Bromo-*p*-tolylnitroamine.*—A solution of 6 g. of 3-bromo-*p*-toluidine in 15 c.c. of acetic acid was added during ½ hour to an ice-cooled mixture of 15 c.c. of acetic acid, 9·3 c.c. of acetic anhydride, and 3·3 c.c. of nitric acid (colourless, *d* 1·50). After a further 15 minutes, the mixture was poured into 900 c.c. of water, and the oil extracted with chloroform. The *nitroamine* was removed from the chloroform extract with 4% sodium carbonate solution, and separated from the more strongly acidic 3-bromo-5-nitro-*p*-tolylnitroamine, which is also formed, by the addition of three-quarters of the calculated quantity of *N*-hydrochloric acid. Yield, 5 g. of white crystals, m. p. 65° after fractional precipitation from sodium carbonate solution and crystallisation from ligroin (b. p. 60—80°) (Found : Br, 34·6. $C_7H_7O_2N_2Br$ requires Br, 34·6%).

2 : 4-Dichlorophenylnitroamine and 2 : 4-*dibromophenylnitroamine* were prepared by the method of Orton (J., 1902, **81**, 806; *Ber.*, 1907, **40**, 370). The latter has m. p. 77° (Found : Br, 53·8. $C_6H_4O_2N_2Br_2$ requires Br, 54·0%).

The preceding nitroamines are highly sensitive to light; in aqueous or aqueous acetic acid solutions a yellow colour due to the isomeric nitroaniline develops rapidly. From the flat colourless crystals of the nitroamine when exposed to light (or to a dry, but acid, atmosphere in the dark), the yellow needles of the nitroaniline grow like a mould; occasionally one yellow needle will grow to a length of several centimetres, with its root in a colourless plate. Both the crystals and the solution may be preserved unchanged for long periods in the dark in the absence of traces of acid.

Medium for Velocity Determination.—" 98% Acetic acid " and " 50% acetic acid " respectively denote that the medium of acetic acid is so diluted by the addition of aqueous mineral acid that the total concentration of water per 100 c.c. of reaction mixture is 2 c.c. or 50 c.c. The hydrochloric, sulphuric, and nitric acids used were the ordinary reagents, the last being colourless but not specially treated to remove traces of nitrous acid. The solution of Kahlbaum's benzenesulphonic acid gave a faint cloudiness with barium chloride solution.

Velocity Measurements.—Since the solution of the nitroamine is colourless, and the nitroaniline is the only coloured product of the transformation, the velocity of transformation is readily determined by colorimetric estimation from time to time of the amount of nitroaniline formed.

For the calculation of the velocity coefficient $k = k_1 + k_2 + \ldots$, the sum of the velocity coefficients for separate side reactions of the first order, the expression $kt = \log_e a/\{a - (1 + r)x\}$ is used, where a = initial concentration of the reactant, x = concentration of one resultant at time t, and r = the ratio of the concentration of the other resultants to the one resultant. If Wegscheider's rule is satisfied, $r = (a - x_\infty)/x_\infty$, and the above expression reduces to $kt = \log_e x_\infty/(x_\infty - x)$, where x_∞ = the concentration of the one resultant at t_∞. The constancy of the values for the velocity coefficients, shown below, calculated by this expression (the nitroaniline being the resultant of which the concentration was measured) provides the foundation for the statement that the transformation of the nitroamines examined involves two or more side reactions of the first order.

In some cases, notably in the transformation of 3-bromo-*p*-tolylnitroamine in 98% acetic acid with 0·02*N*-sulphuric acid, some slow secondary reaction results in the formation of a coloured substance other than the nitroaniline when the main transformation is practically complete; in others the concentration of the nitroaniline as measured colorimetrically reaches a maximum and then slowly falls to the extent of 2 or 3%. It is better in these cases to evaluate x_∞ by a small graphical extrapolation rather than by direct measurement after an "infinitely long" time.

The following description of an actual experiment illustrates the method which, with appropriate modifications, was employed in carrying out the velocity measurements.

*Transformation of 3-Bromo-*p*-tolylnitroamine in 98% Acetic Acid with 0·02N-Hydrochloric Acid.*—To 25 c.c. of a solution of the nitroamine (0·008 g.-mole/litre) and a volume of water such that together with the water in the acetic acid and in the aqueous hydrochloric acid to be added a total volume of 2 c.c. is present, contained in a 100 c.c. flask, sufficient acetic acid was added to make up the volume to about 99 c.c. When the solution had attained the temperature of the thermostat, 20° ± 0·05°, 0·96 c.c. of 2·075*N*-hydrochloric acid was added, the contents of the flask were rapidly mixed by shaking, and the flask was replaced in the thermostat. At intervals, 10 c.c. portions were withdrawn and run into about 80 c.c. of water in a 100 c.c. graduated flask, or at later stages of the reaction, into a mixture of 10 c.c. of acetic acid and about 150 c.c. of water in a 200 c.c. flask, and made up to the mark with water, reaction being almost completely stopped by the cumulative effect of the decrease in concentration of the catalysing acid and the reduction of the acetic acid concentration of the medium brought about by this ten- or twenty-fold dilution. The nitro-

aniline concentration in the diluted solution was estimated colorimetrically.

The Colorimetric Estimation of 3-Bromo-5-nitro-p-toluidine and 2 : 4-Dichloro-6-nitroaniline.—This was carried out with a Leitz colorimeter (1928 model). Illumination by a 100-watt gas-filled lamp screened by two sheets of "daylight" glass, 3 mm. thick, and one sheet of "cobalt" glass, 2 mm. thick, gave a greyish-green colour much easier to match than the original yellow colour of the nitroaniline solutions. Preliminary trials showed that a column of solution of given height matches a column of half the height of a solution of double the concentration, and that variation from 5—15% of acetic acid or 0·0—0·01 mole/litre of mineral acid has no effect on the colour intensity.

The standard procedure throughout these experiments was to dilute the reaction mixture so that 4—8 cm. was colorimetrically equivalent to 6—7 cm. of the standard solutions of 3-bromo-5-nitro-*p*-toluidine or 2 : 4-dichloro-6-nitroaniline in 10% acetic acid containing 0·00005 g.-mole/litre, and to take five independent readings at each of two different settings of the standard. A mean accuracy of ± 1% was obtained. The maintenance of this standard of accuracy throughout a long series of measurements imposes a considerable strain on the observer's eyes.

Experimental Figures.—To illustrate the constancy of the velocity coefficients calculated by the expression $kt = \log_e x_\infty/(x_\infty - x)$, one typical example from each group of experiments is recorded below. The values of k given in the table above (p. 917) are mean values from several concordant experiments. The concentration of the nitroamine is 0·002 g.-mole/litre throughout, and the time is expressed in minutes.

Transformation of 3-Bromo-p-tolylnitroamine in 98% Acetic Acid.

0·02N-Hydrochloric acid.			*0·1N-Hydrochloric acid.*		
Time.	% Nitroaniline.	$k \times 10^3$.	Time.	% Nitroaniline.	$k \times 10^3$.
29·8	19·3	11·0	5·48	21·5	63·7
45·1	26·8	10·9	7·85	29·2	65·1
60·2	33·5	11·0	10·35	35·8	65·2
78·9	40·1	11·0	14·75	44·4	63·5
104	47·1	11·0	18·88	51·2	64·0
∞	69·0	—	∞	73·0	—
	Mean	11·0		Mean	64·3
0·02N-Sulphuric acid.			*0·02N-Benzenesulphonic acid.*		
65·9	19·2	4·95	42·0	19·5	7·91
96·4	26·0	4·90	60·2	26·3	7·97
131	33·0	4·97	84·8	33·6	7·87
187	41·4	4·90	113	40·5	7·83
253	49·4	4·97	145	46·9	7·85
∞	69·0	—	∞	69·0	—
	Mean	4·94		Mean	7·89

Transformation of 3-Bromo-p-tolylnitroamine in 50% Acetic Acid.

N-Hydrochloric acid.			N-Nitric acid.		
Time.	% Nitroaniline.	$k \times 10^3$.	Time.	% Nitroaniline.	$k \times 10^3$.
90·1	24·1	3·89	100·7	25·5	3·73
120	30·2	3·86	141	33·2	3·71
171	40·0	3·95	182	40·2	3·74
226	47·7	3·90	241	48·1	3·70
301	56·7	3·95	321	56·9	3·73
∞	81·5	—	∞	81·5	—
	Mean	3·91		Mean	3·72

Transformation of 2 : 4-Dichlorophenylnitroamine in 98% Acetic Acid.

0·1N-Hydrochloric acid.

Time.	% Nitroaniline.	$k \times 10^3$.
161	17·5	2·33
222	23·0	2·38
291	28·0	2·38
383	33·9	2·43
485	38·1	2·35
∞	56·0	—
	Mean	2·37

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UNIVERSITY COLLEGE OF NORTH WALES,
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CXXI.—*Studies in the Sterol Group. Part III. The Acetylation and Catalytic Hydrogenation of Ergosterol.*

By ISIDOR MORRIS HEILBRON and WILFRED ARCHIBALD SEXTON.

WE suggested in a previous paper, on the evidence adduced from spectrographic results (J., 1928, 47), that two of the ethenoid linkings in ergosterol occupy the same position in the molecule as those in α-cholesterilene, and in a second contribution (*ibid.*, p. 347) it was pointed out that one of the double bonds in the latter compound must be attached to carbon atom 1. In an attempt definitely to establish the existence in ergosterol of a double bond in this position, a study has now been made of its catalytic hydrogenation.

Previous investigators on the hydrogenation of ergosterol have always employed the well-known acetyl derivative in their experiments. This choice does not seem to us altogether happy, because

the acetate is abnormal in that its melting point, values of which have been recorded between 172° and 180°, is higher than that of the free sterol, whereas in the case of cholesterol, sitosterol, and stigmasterol the melting points of the acetates are all lower.

Hydrogenation of the free sterol both in ether at room temperature and in alcohol at 70° in the presence of palladium-black gives rise, when carried to completion, to the α-ergostenol of Reindel and Walter (*Annalen*, 1928, **460**, 212). A study of the rate of addition of hydrogen in ethereal solution revealed a sharp break after the addition of two atoms, and by arresting the process at this stage it has been found possible to isolate in good yield the intermediate dihydroergosterol identical with that obtained by Windaus and Brünken (*Annalen*, 1928, **460**, 225) by the reduction of ergosterol with sodium and alcohol.

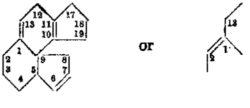
The employment of glacial acetic acid as solvent at a temperature of 70° resulted in the formation of the saturated *allo*-α-ergostanol acetate, identical with that obtained by Reindel and Walter (*loc. cit.*) by hydrogenation of β-ergostenol acetate. Windaus and Linsert (*Annalen*, 1928, **465**, 148) have also brought about the addition of six atoms of hydrogen to ergosterol in hot glacial acetic acid containing a little hydrochloric acid in the presence of platinum-black; these authors do not, however, state the nature of the product.

That the complete saturation of ergosterol under our conditions is not prefaced by any shift of an ethenoid linking prior to hydrogenation has been demonstrated by experiments on the action of acetic acid upon the sterol in an inert atmosphere. These show that acetylation takes place, giving rise to a new acetate (m. p. 132—133°) the absorption spectrum of which is identical with that of ergosterol and of the already well-known acetyl derivative. We consider that this product is the normal acetate of the sterol and consequently propose to designate it as *ergosterol α-acetate*; the acetate prepared by the action of acetic anhydride will be referred to as ergosterol β-acetate. Ergosterol α-acetate yields ordinary ergosterol on hydrolysis with alcoholic potash, and hydrogenation in ethereal solution in the presence of palladium-black converts it into α-ergostenol acetate. The above evidence points to the isomerism between the two being stereochemical: this view is supported by the fact that the α-isomeride changes into the β-form either when heated above its melting point or when boiled with acetic anhydride.

Of the three double bonds in ergosterol, the one which resists hydrogenation in ether or alcohol must be the one which is not present in cholesterilene, since no difficulty is experienced in fully

hydrogenating the latter substance in ether at room temperature. It follows, therefore, from the work of Windaus (*Nach. Ges. Wiss. Göttingen*, Jan., 1926) that in the hydrogenation of ergosterol it should be possible to obtain stereoisomeric forms of both ergostenol and ergostanol. Although only one ergostenol has so far been observed as a direct product of hydrogenation, two ergostanols have been prepared, for hydrogenation of ergosterol in acetic acid gives rise, as pointed out above, to *allo*-α-ergostanol acetate and hydrogenation of ergosterol β-acetate in ethereal solution in the presence of Adams's platinum oxide results in the formation of the isomeric α-ergostanol acetate (Reindel and Walter, *loc. cit.*), which these authors consider differs from its isomeride by asymmetry in the nucleus.

The behaviour of ergosterol on hydrogenation is thus reminiscent of that of abietic acid, where the use of hot glacial acetic acid as solvent is necessary for complete saturation (compare Ruzicka and Meyer, *Helv. Chim. Acta*, 1922, **5**, 315; Ruzicka and Pfeiffer, *ibid.*, 1925, **8**, 632; Madinaveita, *Chem. Abstr.*, 1923, **17**, 288). The resistant double bond in this case joins two quaternary carbon atoms, and we venture tentatively to suggest by analogy that in ergosterol the third double bond may be similarly disposed. Such a position is to be found between carbon atoms 10 and 11 (see formula, where a suggested nuclear structure is shown). With regard to this possibility, attention must be directed to the recent work of Wieland and Vocke on the bile acids (*Z. physiol. Chem.*, 1928, **177**, 68). These authors consider that their results indicate the presence of a methyl group attached to carbon 11 (see also *Ann. Reports*, 1928, **25**, 162). In such a case the resistant double bond may be between carbon atom 10 and the side chain bearing carbon atom 19.



Experimental.

Hydrogenation of Ergosterol in Ether and in Alcohol.—Ergosterol (1 g.) was dissolved in dry ether (150 c.c.) and hydrogenated at a pressure slightly greater than atmospheric in the presence of palladium-black (1 g.). The solution was filtered from the catalyst and, after addition of about one-third of its volume of methyl alcohol, left in a covered beaker to crystallise. The first crop (0·5 g.) consisted of flat needles, m. p. 128—130°. Re-

crystallisation from ether–methyl alcohol gave a product, m. p. 130—131°, the value recorded in the literature for α-ergostenol. The second crop (0·2 g.), third crop (0·1 g.), and fourth crop (0·1 g.) all consisted of less pure forms of the same substance.

Ergosterol (2 g.) was dissolved in absolute alcohol (150 c.c.) at 70° and hydrogenated for 5 hours in the presence of palladium-black. The filtered solution was concentrated and allowed to crystallise. The first crop (0·5 g.) melted at 122—126°, the second (0·5 g.) at 125—127°, and the third (0·2 g.) at 116—124°. (The loss of material is attributed to its absorption by the palladium.) The three crops were combined and recrystallised from ether–methyl alcohol, giving flat needles, m. p. 130—131°, showing no depression in admixture with the α-ergostenol prepared by hydrogenation in ethereal solution.

Dihydroergosterol.—Ergosterol (5 g.) was dissolved in ether (400 c.c.) and hydrogenated in the presence of palladium-black (2 g.) until 350 c.c. of hydrogen were absorbed (calc. for one double bond, 295 c.c.). Excess of hydrogen was purposely used, as the separation of traces of ergosterol from dihydroergosterol is a tedious process, whereas α-ergostenol may be removed from dihydroergosterol by crystallisation with comparative ease. The product was fractionally crystallised from ether–methyl alcohol and the first two crops were combined (3·2 g.) and repeatedly crystallised from alcohol. Dihydroergosterol was thus obtained in plates, m. p. 173°, $[\alpha]_{5461}^{20^\circ}$ −21·7° (*c* = 1·248 in chloroform). The acetate, prepared by the action of acetic anhydride, melted at 180° [Windaus and Brünken (*loc. cit.*) give for dihydroergosterol m. p. 173—174°, $[\alpha]_D$ −19°, and for the acetate m. p. 180—181°]. The third and fourth crops (1·5 g.) consisted of α-ergostenol.

allo-*α-Ergostanol Acetate.*—Ergosterol (1 g.) was dissolved in glacial acetic acid (120 c.c.), and the solution hydrogenated at 70° in presence of palladium-black (1 g.) for 8 hours. The resulting colourless solution was decanted from the catalyst, diluted with water, and extracted with ether. The ethereal extract, after being washed with dilute alkali solution and with water, was mixed with methyl alcohol (⅓ vol.) and kept in a covered beaker, crops of crystals being removed from time to time. The first crop (0·4 g.) consisted of flat needles, m. p. 120—129°. Recrystallisation from ether–methyl alcohol gave a constant m. p. of 144—145° (Reindel and Walter, *loc. cit.*, give 145°) [Found : (micro) C, 81·0; H, 11·8. Calc. for $C_{29}H_{50}O_2$: C, 80·9; H, 11·6%].

allo-*α-Ergostanol.*—The acetate (1 g.) was refluxed for 1 hour with 10% alcoholic potash (100 c.c.): crystalline plates separated on cooling. Repeated crystallisation from ether–methyl alcohol

gave a m. p. of 144° (Reindel and Walter, *loc. cit.*, give 144—145°). The substance was dried at 100° [Found: (micro) C, 80·3; H, 12·5; H_2O, 3·8. Calc. for $C_{27}H_{48}O,H_2O$: C, 80·2; H, 12·4; H_2O, 4·4%. Reindel, Walter, and Rauch (*Annalen*, 1927, **452**, 34) found "about" 1 H_2O].

Ergosterol α-*Acetate*.—A solution of ergosterol (2 g.) and anhydrous potassium acetate (5 g.) in glacial acetic acid (200 c.c.) was maintained at 100° for 5—6 hours, a stream of carbon dioxide being passed through the flask to minimise any loss by atmospheric oxidation. The crystals which separated on cooling (1·0 g.) contained a considerable amount of unchanged sterol. The filtrate was poured into water, and the product extracted with ether. The washed and dried extract was evaporated, and the residue purified by repeated crystallisation from absolute alcohol. The α-*acetate* formed small leaves, m. p. 132—133° [Found: (micro) C, 81·8; H, 10·8. $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4%].

A further quantity of the acetate was recovered by fractional crystallisation of the first crop from alcohol–ether, the acetyl derivative being found in the more soluble portion. The acetylation can also be carried out in the absence of potassium acetate; nevertheless the presence of this substance is desirable. In some cases a product, m. p. 133°, was obtained which was shown by analysis to contain unchanged ergosterol. This is probably a eutectic mixture of the sterol and the acetyl derivative.

Conversion of Ergosterol α-*Acetate into the* β-*Isomeride*.—Ergosterol α-acetate (1 g.) was heated under reflux for 1 hour with acetic anhydride (4 c.c.), and the product treated with alcohol to destroy the excess of the anhydride. On recrystallisation of the resulting compound from absolute alcohol, the characteristic leaves of ergosterol β-acetate (m. p. 172—174°) separated. The conversion was also brought about by maintaining the molten compound for ½ hour at 170—180° and repeatedly recrystallising the product from absolute alcohol.

Hydrogenation of Ergosterol α-*Acetate*.—The acetate (1·2 g.) was dissolved in ether (100 c.c.) and hydrogenated in the presence of palladium-black until absorption of hydrogen ceased. The volume absorbed was 135 c.c. (N.T.P.) (Calc. for 2 mols. of hydrogen, 127 c.c.). The product after repeated crystallisation from ether–methyl alcohol had m. p. 109—110° and gave no depression in admixture with α-ergostenol acetate prepared by acetylation of the free alcohol.

Hydrolysis of Ergosterol α-*Acetate*.—The acetate (1·5 g.) was refluxed for an hour with 5% alcoholic potash (100 c.c.), and the solution allowed to cool. The crystals obtained melted after

recrystallisation at 160° and gave no depression in admixture with ergosterol.

We desire to express our thanks to Mr. F. S. Spring, B.Sc., *for* his help in a portion of the experimental work.

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CXXII.—*Studies in the Sterol Group. Part IV. The Existence of Isomeric Ergosterols.*

By ISIDOR MORRIS HEILBRON, WILFRED ARCHIBALD SEXTON, and FRANK STUART SPRING.

IT was shown by Heilbron and Sexton (preceding paper) that the hydrogenation of yeast ergosterol in ethereal solution in the presence of palladium leads to the formation of the tetrahydro-derivative, α-ergostenol. The ergosterol employed in those experiments was prepared by Böhringer und Söhne of Hamburg. In a continuation of that work, a yeast ergosterol supplied by Messrs. Boot (Boot's *A*) was used, but to our surprise, working under identical conditions, we failed to obtain α-ergostenol, the reaction ceasing after the addition of approximately two atoms of hydrogen (compare Curves I *and II*).

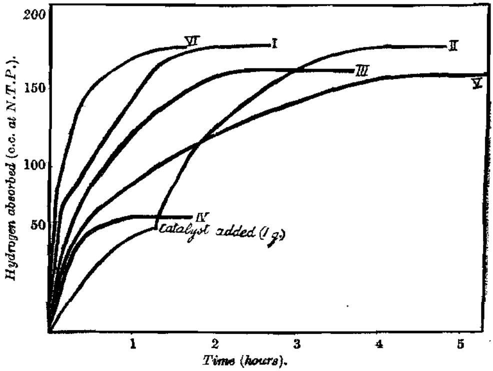
The first explanation which suggested itself to us was the presence of a catalyst poison in Boot's ergosterol. In order to test this, Boot's ergosterol was hydrogenated in ethereal solution until addition of hydrogen had ceased. The same catalyst was then employed with success in the hydrogenation of fresh Böhringer ergosterol, α-ergostenol being readily obtained with no diminution of the rate of absorption of hydrogen.

The homogeneity of the two sterols was demonstrated by fractionally crystallising each of them three times under identical conditions from the alcohol-benzene solvent recommended by Bills and Honeywell (*J. Biol. Chem.*, 1928, **80**, 15). The last two crystallisations effected no alteration of specific rotation, the melting points of the two sterols were identical at each stage, and no depression was noted in mixtures of them. The pure Boot's ergosterol had $[\alpha]_{5461}^{22^\circ}$ $-171°$, and the Böhringer product $[\alpha]_{5461}^{20^\circ}$ $-159·3°$. The absorption spectra of the two sterols showed the same characteristic absorption bands in the ultra-violet region. The extinction coefficients were, however, slightly different, the ratio being of the order 1·2 (Böhringer product) : 1·0 (Boot's sterol). As the ergosterol showing the higher extinction coefficient has the

lower specific rotation, it follows that, if Boot's ergosterol contains a non-absorbing impurity, this must have an exceptionally high lævorotation: the sterol commonly associated with ergosterol (zymosterol), however, is actually dextrorotatory (Smedley-Maclean, *Biochem. J.*, 1928, **22**, 22).

Hydrogenation of the purified Böhringer sterol gave α-ergostenol in the normal manner (Curve I), whereas the hydrogenation of the purified Boot's sterol proceeded in the same manner as that of the

FIG. 1.



I. *Böhringer's ergosterol* (1·5 *g.*) *with* 1 *g. of catalyst.*
II. *Boot's A ergosterol* (1·5 *g.*) *with* 1 *g. of catalyst and subsequent addition of* 1 *g. of catalyst.*
III. *Böhringer's ergosterol acetate with* 1 *g. of catalyst.*
IV. *Boot's A ergosterol acetate with* 1 *g. of catalyst.*
V. *Boot's A ergosterol acetate with* 2 *g. of catalyst.*
VI. *Boot's B ergosterol with* 2 *g. of catalyst.*

crude material. The more soluble portion of each preparation, obtained by evaporation of the filtrate from the first crystallisation, behaved in the same way on hydrogenation as the less soluble fraction. The quantity of hydrogen absorbed by Boot's ergosterol was slightly less than the volume required for complete saturation of one ethenoid linking. Attempts were made, however, to ascertain whether, as found in the case of Böhringer's sterol (Heilbron and Sexton, *loc. cit.*), pure dihydroergosterol could be isolated from the product; but these were unsuccessful, as ergosterol was still present.

On the other hand, we were invariably able to complete the hydrogenation to tetrahydroergosterol by the addition of more catalyst at this stage, but, as shown in Curve II, the reaction was very slow. An examination of the product obtained under these conditions revealed a marked difference, for whereas Böhringer's ergosterol gave rise solely to α-ergostenol, the tetrahydro-derivative from Boot's sterol was separable into α- and β-ergostenols. The isolation of the β-isomeride in this way is at first sight curious, as Reindel and Walter (*Annalen*, 1927, **460**, 212) have shown that β-ergostenol acetate is hydrogenated without difficulty in the presence of platinum to the saturated *allo*-α-ergostanol acetate. Experiments carried out by us, however, on free β-ergostenol with a palladium catalyst showed that the reaction was difficult to carry to completion.

A series of experiments was also carried out with twice the initial amount of catalyst, in order to see whether four atoms of hydrogen could be directly added to Boot's ergosterol. Unfortunately, a fresh supply of the sterol (Boot's B) was used which, after purification as already described, had a specific rotation $[\alpha]_{5461}^{22^\circ}$ $-161{\cdot}2^\circ$. Four atoms of hydrogen were absorbed with no marked break at the dihydro-stage (Curve VI). It was sometimes difficult to free the product entirely from dihydroergosterol, and although α-ergostenol was readily isolated, we failed to obtain evidence of the formation of the β-isomeride.

The two sterols, Böhringer's and Boot's A, were each converted into the β-acetates (Heilbron and Sexton, *loc. cit.*) by means of acetic anhydride. Although the two acetates had identical melting points and specific rotations, Curve IV shows that the difficulty of hydrogenating Boot's sterol persists after acetylation. Both in this case and also when a large initial excess of catalyst was used (Curve V) we failed to detect β-ergostenol acetate, the α-isomeride alone being isolated. It may well be, however, that β-ergostenol acetate was formed in small quantity, but could not be separated from the α-compound. Hydrolysis of Boot's A acetate with alcoholic potash gave a sterol which after purification had a specific rotation $[\alpha]_{5461}^{22^\circ}$ -160°, the value for the Böhringer product. On hydrogenation this hydrolysed material behaved precisely as the original Böhringer ergosterol, the velocity break appearing at the dihydro-stage and α-ergostenol being the sole product. It is thus possible by acetylation and hydrolysis to convert Boot's ergosterol into an ergosterol the behaviour of which on hydrogenation is in harmony with the recorded result of previous workers, and the failure of previous investigators to observe the results described above may be due to their having subjected the ergosterol to a

purification process involving acetylation and hydrolysis (compare Reindel and Walter, *loc. cit.*).

The melting point of ergosterol β-acetate recorded by various investigators shows considerable discrepancies, *e.g.*, 170—172° by Reindel and Walter (*loc. cit.*) and 180° by Bills and Honeywell (*loc. cit.*). We have found that the melting point is dependent on the duration of the treatment with acetic anhydride: the longer the treatment, the lower is the m. p. and the higher the specific rotation. Heilbron, Morton, and Sexton (J., 1928, 37) have directed attention to the susceptibility of the sterol nucleus to racemisation, and we regard it as probable that under the rather violent conditions of its preparation ergosterol β-acetate undergoes partial racemisation, giving rise to the observed difference in physical constants.

All the ergosterols so far examined are converted on irradiation into vitamin-*D*.

EXPERIMENTAL.

Fractionation of Böhringer's and of Boot's A Ergosterols.—Each sterol (25 g.) was dissolved in 500 c.c. of a boiling mixture of industrial alcohol (2 parts) and benzene (1 part), and the filtered solution kept over-night; the ergosterol had then crystallised in glistening flat needles. These were removed and the filtrate was concentrated to half its bulk to obtain a second crop. The first crop was recrystallised twice from the same proportion of solvent and the m. p. and the specific rotation of the products were determined at each stage. These are shown, together with the weights of the crops, in the table.

		Boot's A.		Böhringer.	
Fraction.	Wt. (g.).	M. p.	$[\alpha]_{5461}^{21\cdot5^\circ}$.	M. p.	$[\alpha]_{5461}^{21\cdot5^\circ}$.
Crude	25·0	158—159°	−155°	158—159°	−145·3°
1st Cryst.	18·5	160—161	−171·2	160—161	−159·2
2nd ,,	13·2	160·5—161·5	−171·0	160·5—161·5	−159·2
3rd ,,	9·5	161—162	−171·0	161—162	−159·3
2nd crop from filtrate of 1st crystallisation	5·0	157—159	−150·0	158—159	−134·5

Catalytic Hydrogenation.—The hydrogenations were all carried out in presence of palladium-black prepared by a modification of Seng's method (Diss., Göttingen, 1918), for which we are indebted to Mr. W. Doran, M.Sc.

Palladous chloride (1 g.) was digested with water (1000 c.c.) on a steam-bath for 1 hour with continual stirring. Formic acid (2 c.c. of 80%) was then added to the hot solution, followed after 5 minutes by a solution of potassium hydroxide (50 c.c. of 10%). The liquid was kept on the steam-bath with continual stirring for

2 hours and the precipitated palladium was then filtered off, thoroughly washed with hot water, and dried over calcium chloride in a desiccator.

Hydrogenation of Böhringer's Ergosterol.—The sterol (1·5 g.) was dissolved in ether (250 c.c.) and hydrogenated in the presence of the catalyst (1 g.), conversion into the tetrahydro-derivative being effected in 1½—2 hours. The product (m. p. 126°), after twice crystallising from ether–methyl alcohol, had m. p. 130—131° and $[\alpha]_{5461}^{22°}$ +18·0° (*c* = 1·104 in chloroform). The rate of addition of hydrogen is indicated in Curve I, where the velocity break at the dihydro-stage is evident.

Hydrogenation of Boot's A Ergosterol.—Under precisely the same conditions as those described above, the absorption of hydrogen had almost ceased after 80 minutes (Curve II) (Found: H_2 absorbed, 65 c.c. Calc. for one double bond, 88 c.c.). At this stage fresh catalyst was added (1 g.); the absorption of hydrogen was then resumed and continued slowly until the tetrahydro-stage was reached. The filtered solution was concentrated to half its bulk, treated with a little methyl alcohol, and kept in a covered beaker. The first crop (0·5 g.) melted at 114° and on further crystallisation the m. p. could not be raised above 114—116°. On treatment with acetic anhydride, it gave β-ergostenol acetate which, alone or mixed with β-ergostenol acetate prepared by Reindel, Walter, and Rauch's method (*Annalen*, 1927, **452**, 34), melted at 94—96°. The second crop (0·8 g.) melted at 126°, and at 130—131° after several recrystallisations from ether–methyl alcohol. It then had $[\alpha]_{5461}^{21°}$ +19° (*c* = 1·104 in chloroform) and showed no depression of m. p. when mixed with α-ergostenol prepared from Böhringer's ergosterol.

Acetylation of the Ergosterols with Acetic Anhydride.—Boot's A sterol (1 g.) was heated at 135—145° with acetic anhydride for various times, and the product recrystallised from ether–acetone (1 : 3). The physical constants were as follows:

Time of treatment (mins.)	10	30	90
$[\alpha]_{5461}^{21°}$	−109·0°	−115·6°	−119·3°
M. p.	176—177°	172—174°	171—173°

A purified sample of Böhringer's ergosterol, after being treated for 30 minutes, gave exactly the same m. p. and specific rotation as Boot's isomeride.

Hydrogenation of the β-Acetates.—The same quantities were employed as in the case of the free sterols. Curve III represents the addition of hydrogen to the Böhringer acetate, and Curves IV and V show the rate of hydrogenation of the Boot acetate. The product in each case consisted entirely of α-ergostenol acetate,

which after two crystallisations from ether–methyl alcohol had m. p. 109—110° and $[\alpha]^{21°}_{5461}$ +6·3° (c = 1·74 in chloroform).

Hydrolysis of Ergosterol β-Acetate.—Boot's ergosterol β-acetate (m. p. 172—174°) (5 g.) was refluxed with 5% alcoholic potash (100 c.c.) for 1 hour. The product which separated on cooling was recrystallised from alcohol–benzene; it then had m. p. 161—162° and $[\alpha]^{21°}_{5461}$ −160·0° (c = 1·194 in chloroform). Hydrogenation of this ergosterol (1·5 g.) in the presence of palladium-black (2 g.) was complete in about 1 hour. After two recrystallisations of the crude product from ether–methyl alcohol, pure α-ergostenol, m. p. 130—131°, $[\alpha]^{22°}_{5461}$ +19° (c = 1·74 in chloroform), was obtained.

Hydrogenation of β-Ergostenol.—β-Ergostenol (0·5 g.), prepared by Reindel, Walter, and Rauch's method (*loc. cit.*), was hydrogenated in the presence of palladium-black (2 g.) until absorption of hydrogen ceased (21 c.c.) (Calc. *for one double bond* : 29 c.c.). The product when tested by the Liebermann–Burchard reaction gave a strong colour indicating the presence of unsaturated material.

Hydrogenation of Boot's B Ergosterol.—The sterol (1·5 g.), which had $[\alpha]^{22°}_{5461}$ −161·2° (c = 2·1 in chloroform), was hydrogenated in the presence of palladium (2 g.), absorption of 4 atoms being complete in 1½ hours (Curve VI). The product was fractionally crystallised from ether–methyl alcohol in the usual manner. The first four crops (1·2 g.) consisted of impure α-ergostenol (m. p. 124—126°). One crystallisation of the combined crops from ether–methyl alcohol gave a substance having m. p. 129—131° and showing no depression in m. p. when mixed with an authentic specimen of α-ergostenol.

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CXXIII.—*The Intermolecular Condensation of Styryl Ketones. Part III. Further Examples of the Ready Formation of Bis-(Styryl Ketones).*

By ISIDOR MORRIS HEILBRON and FRANCIS IRVING.

IN a previous communication (Heilbron and Irving, J., 1928, 2323), an account was given of the formation of bis-(styryl nonyl ketones). We have now investigated the interaction of benzaldehyde with methyl *n*-propyl ketone and higher homologues up to methyl *n*-octyl ketone and find that in all cases both the simple styryl ketone and its dimeride can be obtained. In the branched-chain series, only four ketones have been examined and of these methyl *iso*butyl and methyl *iso*hexyl ketones yield dimerides, but methyl *iso*propyl ketone and pinacolin fail to do so. Some of the

dimerides have been obtained by previous workers without, however, their identity having been recognised. For instance, *bis-(styryl* n-*propyl ketone)* was actually prepared by Vorländer (*Ber.*, 1897, **30**, 2267), but was regarded by him as a complex triketone; other similar examples are dealt with in the experimental portion.

The styryl ketones are readily distinguished from their bis-forms by the very wide difference in melting point which exists between them and also by the fact that, whereas the former separate in well-defined crystals, the dimerides usually form masses of felted needles (cotton-wool appearance). These points are well exemplified in the case of methyl *n*-hexyl ketone, where the simple styryl derivative crystallises in definite plates, m. p. 32—33°, and the *dimeride* forms clusters of hair-like needles, m. p. 152°. Similarly, 4-*methoxystyryl hexyl ketone* has m. p. 55°, whereas the dimeride melts at 145—146°.

Among the straight-chain dimerides, a certain regularity in melting point is apparent, increase in the length of the carbon chain by a methylene group causing a lowering of m. p. of approximately 13°. In the cases so far examined, the branched chain dimerides have higher m. p.'s than the corresponding straight-chain isomerides.

In connexion with the above melting points an investigation by Rupe and Wild (*Annalen*, 1916, **414**, 111) comes under review. These authors prepared the active and the inactive forms of amylacetone (ε-methylheptan-β-one, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3$) and condensed them with benzaldehyde and with anisaldehyde. The styryl γ-methylamyl ketones were obtained as colourless, felted needles, m. p. 139° (active) and 173° (inactive). On the other hand, 4-methoxystyryl γ-methylamyl ketone (active) is described as forming large, pearly scales, m. p. 55°. There can be little doubt from these descriptions that, whereas the two former compounds are actually dimerides and thus wrongly designated, the latter is correctly named. In support of this contention it is of interest to note that Rupe and Wild unexpectedly obtained a higher rotation value for the compound of m. p. 139° ($\alpha_D^{20^\circ}$ +10·77°) than for that of m. p. 55° ($\alpha_D^{20^\circ}$ +8·62°), and mention that the anomaly " bedarf noch weiterer Untersuchung "; in view, however, of the facts now pointed out, the explanation is self-evident.

As regards the formation of the bis-compounds, we have found that (*a*) the higher members of the series are the more easily produced and (*b*) a substituted aldehyde gives rise to a dimeride less readily than benzaldehyde itself. Further, as already mentioned, dimerides are only formed from branched-chain ketones when at least one methylene group separates the branch radical from the carbonyl group—a fact which points to steric hindrance, especially

on the basis of the dimerides being *cyclo*butane derivatives (compare Heilbron and Irving, *loc. cit.*). In no case has the formation of a *cyclo*hexenone derivative, snch as was obtained from 3 : 4-dimethoxystyryl methyl ketone (Dickinson, Heilbron, and Irving, J., 1927, 1888), been observed, and it may be concluded that this only occurs when the styryl ketone has a terminal methyl radical.

The solvent appears to be one of the main factors determining the formation of the mono- or the bis-form during the condensation. In aqueous alcohol (60—70%), the styryl ketone itself is formed, probably owing to its ready separation and consequent removal from the action of the alkali; but when absolute alcohol is employed, the dimeride is produced even under the same conditions of alkali concentration.

The dimerides of the higher members of the series may prove useful in the identification of the ketones, since they are very easily prepared and have high melting points.

EXPERIMENTAL.

Styryl *n*-propyl ketone has been prepared by Harries and Bromberger (*Ber.*, 1902, **35**, 3088), and is a liquid at the ordinary temperature.

Bis-(Styryl n*-Propyl Ketone).*—A solution of benzaldehyde (21 g.) and methyl *n*-propyl ketone (17 g.) in absolute alcohol (100 c.c.) was treated with 10% sodium hydroxide solution (15 c.c.) and kept at room temperature for 2 days; crystals then began to separate. After 4 days, these were recrystallised from alcohol–ethyl acetate, small, colourless, glistening needles being obtained, m. p. 194—195° (Vorländer, *loc. cit.*, gives 197°). The compound dissolved in concentrated sulphuric acid to a yellow solution, and failed to decolorise a solution of bromine in chloroform [Found : C, 82·9, 82·8; H, 8·2, 8·2; *M* (Menzies), 350, 347. $C_{24}H_{28}O_2$ requires C, 82·8; H, 8·1%; *M*, 348].

Styryl *n*-butyl ketone (m. p. 38—39°) has been prepared by Auwers and Voss (*Ber.*, 1909, **42**, 4421) by condensing benzaldehyde with methyl *n*-butyl ketone in presence of alkali and has also been obtained by an indirect method by Mayer (*Bull. Soc. chim.*, 1905, **33**, 397).

Bis-(Styryl n*-Butyl Ketone).*—A solution of methyl *n*-butyl ketone (12 g.) and benzaldehyde (12·5 g.) in absolute alcohol (90 c.c.) was treated with 30% sodium hydroxide solution (8 c.c.) at room temperature, crystals beginning to separate after 12 hours. The product, after 4 days' standing, crystallised from ethyl acetate in fine, colourless needles, m. p. 175—176° (Found : C, 83·0; H, 8·7; *M*, 383. $C_{26}H_{32}O_2$ requires C, 83·0; H, 8·7%; *M*, 376).

Bis-(Styryl iso*Butyl Ketone).*—Gheorghiu and Arwentiew (*J. pr. Chem.*, 1928, **118**, 295), on condensing benzaldehyde with methyl *iso*butyl ketone in presence of alkali, obtained the liquid styryl *iso*butyl ketone, together with a small amount of a product, m. p. 197°, which they regarded as an isomeride or a polymeride. We find this compound to be dimeric styryl *iso*butyl ketone and have obtained it both by the method of these authors and also by the following processes: (1) A solution of benzaldehyde (25 g.) and methyl *iso*butyl ketone (24 g.) in absolute alcohol (170 c.c.) was treated with 25% sodium hydroxide solution (15 c.c.) and kept at room temperature for 7 days. The product, after being washed with alcohol, crystallised from alcohol–ethyl acetate in colourless needles, m. p. 202° (yield, 6·5 g.). (2) A solution of styryl *iso*butyl ketone (5 g.) in absolute alcohol (40 c.c.) was treated with 25% sodium hydroxide solution (10 c.c.) and kept at room temperature for 7 days, crystals of the dimeride slowly separating (yield, 0·8 g.). The compound gives a slightly yellow solution in concentrated sulphuric acid and fails to decolorise a solution of bromine in chloroform (Found: C, 83·1; H, 8·7; *M*, 379. $C_{26}H_{32}O_2$ requires C, 83·0; H, 8·5%; *M*, 376).

*Bis-(4-*iso*Propylstyryl* iso*Butyl Ketone).*—A solution of cuminal (4·5 g.) and methyl *iso*butyl ketone (3 g.) in alcohol (20 c.c.) was first treated with 15% sodium hydroxide solution (2 c.c.) and then, after 1 day, with 30% sodium hydroxide solution (1 c.c.). The whole was left for 8 days, and the product then crystallised from alcohol–ethyl acetate. The same product was obtained by allowing the same quantities of aldehyde and ketone, dissolved in alcoholic potassium hydroxide (22 c.c. of 4%), to remain at room temperature for 4 weeks. *Bis-(4-*iso*propyl* iso*butyl ketone)* forms colourless, glistening, hair-like needles, m. p. 192—194° (Found: C, 83·2; H, 9·6; *M*, 473. $C_{32}H_{44}O_2$ requires C, 83·5; H, 9·6%; *M*, 460).

Unsuccessful attempts were made to obtain dimerides by the condensation of methyl *iso*butyl ketone with piperonal, veratraldehyde, and *p*-chlorobenzaldehyde.

Styryl *n*-hexyl ketone (m. p. 34°) has been described by Mayer (*loc. cit.*; *Bull. Soc. chim.*, 1916, **19**, 431), who obtained it by allowing methyl *n*-hexyl ketone to react with benzylideneaniline and decomposing the product with sulphuric or acetic acid. We have now prepared the ketone by direct alkali condensation in the following manner: Benzaldehyde (2 g.) and methyl *n*-hexyl ketone (2·2 g.) were dissolved in 60 c.c. of 70% alcohol containing 0·3 g. of potassium hydroxide. After standing at room temperature for 2 days, the pale yellow solution was slightly diluted; a pale yellow oil, which solidified on freezing, then separated. Recrystallisation from

methyl alcohol in a freezing mixture gave faintly yellow plates, m. p. 32—33°.

Bis-(Styryl n-*Hexyl Ketone).*—A solution of benzaldehyde (2 g.) and methyl *n*-hexyl ketone (2·2 g.) in absolute alcohol (10 c.c.) was mixed with sodium hydroxide (1 c.c. of 30%) and kept over-night at room temperature. The separated product was washed with alcohol and repeatedly crystallised from alcohol–ethyl acetate. The *dimeride* separated in fine matted needles, m. p. 152° (Found: C, 83·3; H, 9·5; *M*, 442. $C_{30}H_{40}O_2$ requires C, 83·3; H, 9·3%; *M*, 432).

4-*Methoxystyryl* n-*Hexyl Ketone.*—A solution of anisaldehyde (2 g.) and methyl *n*-hexyl ketone (2 g.) in alcohol (12 c.c.) was treated with sodium hydroxide (8 c.c. of 1%) and kept at room temperature for a few hours; a yellow oil, which solidified on cooling in the ice-chest, then separated. The pure *ketone* separated from methyl alcohol in colourless plates (pearly scales from aqueous methyl alcohol), m. p. 55° (Found: C, 77·9; H, 9·1. $C_{16}H_{22}O_2$ requires C, 78·0; H, 8·9%).

Bis-(4-Methoxystyryl n-*Hexyl Ketone).*—The same quantities of anisaldehyde and methyl *n*-hexyl ketone as were used in the previous experiment were dissolved in 3% alcoholic potassium hydroxide, and the solution heated under reflux for 4 hours. The product crystallised from alcohol in fine, colourless, felted needles, m. p. 145—146°. Attempts to form this *dimeride* by working at the ordinary temperature were unsuccessful (Found: C, 77·9; H, 9·0; *M*, 512. $C_{32}H_{44}O_4$ requires C, 78·0; H, 8·9%; *M*, 492).

Bis-(Styryl iso*Hexyl Ketone).*—A solution of benzaldehyde (5 g.) and methyl *iso*hexyl ketone (5·5 g.) in absolute alcohol (25 c.c.) was kept for 12 hours at room temperature in presence of sodium hydroxide (2·5 c.c. of 30%). The separated product crystallised from alcohol–ethyl acetate in fine, colourless, matted needles, m. p. 177° (Found: C, 83·4; H, 9·5; *M*, 436. $C_{30}H_{40}O_2$ requires C, 83·3; H, 9·3%; *M*, 432).

Styryl *n*-heptyl ketone (m. p. 52°) has been prepared by Mayer (*loc. cit.*) by the indirect method to which reference has already been made. It can, however, be obtained with ease by direct alkali condensation in the following manner: Benzaldehyde (2 g.) and methyl *n*-heptyl ketone (2·7 g.) were dissolved in 75% alcohol (60 c.c.) containing 0·3 g. of potassium hydroxide. The product commenced to separate in a few hours, and after 2 days colourless leaflets of the pure ketone (m. p. 51—52°) were obtained (yield, 3 g.); the filtrate slowly deposited a small quantity of the dimeride described below.

Bis-(Styryl n-*Heptyl Ketone).*—A solution of benzaldehyde (4 g.)

and methyl *n*-heptyl ketone (5·6 g.) in absolute alcohol (20 c.c.) was treated with 30% sodium hydroxide solution (0·8 c.c.) and kept at room temperature for 5 days. After repeated crystallisation from absolute alcohol, the *dimeride* was obtained in fine, matted, colourless needles, m. p. 144° (Found: C, 83·5; H, 9·5; *M*, 466. $C_{32}H_{44}O_2$ requires C, 83·5; H, 9·6%; *M*, 460).

Styryl n-Octyl Ketone.—Benzaldehyde (2 g.) and methyl *n*-octyl ketone (3 g.) were dissolved in alcohol (60 c.c. of 75%) containing 0·2 g. of potassium hydroxide, and the solution kept at room temperature for 2 days. The product was recrystallised from methyl alcohol in a freezing mixture, the pure *ketone* separating in pale yellow leaflets, m. p. 38—39° (Found: C, 83·8; H, 10·0. $C_{17}H_{24}O$ requires C, 83·6: H, 9·8%).

Bis-(Styryl n-*Octyl Ketone).*—A solution of benzaldehyde (4·1 g.) and methyl octyl ketone (6 g.) in absolute alcohol (20 c.c.) was treated with sodium hydroxide solution (0·2 c.c. of 30%), clusters of fine needles gradually separating. After 4 days the product was collected and recrystallised from absolute alcohol, a felted mass of very fine, colourless needles being obtained, m. p. 131·5° (yield, 0·9 g. of pure substance) (Found: C, 83·7; H, 9·7; *M*, 487. $C_{34}H_{48}O_2$ requires C, 83·6; H, 9·8%; *M*, 488).

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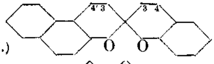
CXXIV.—*Styrylpyrylium Salts. Part XI. The Determination of the Reactive Group in Ketones of the Type* $CH_3·CO·CH_2R$ *by Means of the Benzo-β-naphtha*spiro*pyran Colour Change.*

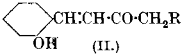
By ISIDOR MORRIS HEILBRON and FRANCIS IRVING.

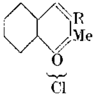
IT is generally accepted that in aldehyde–ketone condensations in which the ketone contains both a methyl and a methylene group the former or the latter is reactive according as an alkali or an acid is used as the condensing agent (compare Goldschmiedt and Knöpfer, *Monatsh.*, 1897, **18**, 437; 1898, **19**, 406; Harries and Müller, *Ber.*, 1902, **35**, 966; Harries and Bromberger, *ibid.*, p. 3088; Auwers, *Ber.*, 1912, **45**, 2764). For instance, from salicylaldehyde and a ketone of the type $CH_3·CO·CH_2R$ alkali condensation would produce (II), from which (IV) is obtained by the action of hydrogen chloride, isomeric with (III) formed by direct acid condensation (compare Decker and Fellenberg, *Annalen*, 1909, **364**, 1).

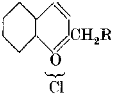
By further condensation of (III) and (IV) with 2-naphthol-1-

aldehyde, the isomeric 3- and 3′-substituted benzo-β-naphtha*spiro*-pyrans are respectively obtained (I).

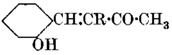
(I.) 

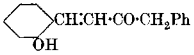
 (II.)

(III.) 

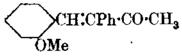
 (IV.)

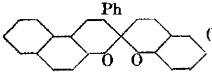
It has been shown that, whereas benzo-β-naphtha*spiro*pyrans substituted in the 3-position ionise on being heated in inert solvents, giving coloured solutions, the isomeric 3′-substituted compounds fail to show this phenomenon (Dickinson and Heilbron, J., 1927, 1699). This reaction can therefore be utilised in deciding between the structures (II) and (V), and affords a readier method than the oxidation and reduction reactions used previously (compare Goldschmiedt and Krczmar, *Monatsh.*, 1901, **22**, 659; Harries and Müller, *loc. cit.*; Harries and Bromberger, *loc. cit.*; Stoermer and Wehln, *Ber.*, 1902, **35**, 3549: Gheorghiu and Arwentiew, *J. pr. Chem.*, 1928, **118**, 295).

(V.) 

 (VI.)

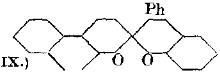
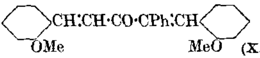
In order to illustrate this method for the determination of structure we have again examined the ketone obtained by Dickinson (J., 1926, 2234), by condensing salicylaldehyde with benzyl methyl ketone in presence of piperidine. This compound (A) was regarded as 2-hydroxystyryl benzyl ketone (VI), since its methyl derivative was not identical with the *ketone* (B) prepared by condensing *o*-methoxybenzaldehyde with benzyl methyl ketone by means of hydrogen chloride, which from analogy with known reactions was designated 2-methoxy-α-phenylstyryl methyl ketone (VII).

(VII.) 

 (VIII.)

We have now prepared the phenylbenzo-β-naphtha*spiro*pyran from (A) and find that it develops a purple colour in boiling xylene and other higher-boiling inert solvents, and also that it differs in melting point from the isomeric, non-ionising *spiro*pyran obtained by Dilthey, Berres, Hölterhoff, and Wübken (*J. pr. Chem.*, 1926, **114**,

179). *From its method of preparation the latter compound must* have the structure (VIII), and consequently the *spiro*pyran derived from (A) must be *3-phenylbenzo-β-naphtha*spiro*pyran* (IX).

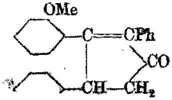
(IX.)   (X.)

The same compound is obtained by condensing the pyrylium salt (III; R = Ph), *prepared from* salicylaldehyde and benzyl methyl ketone, with 2-naphthol-1-aldehyde. The effect of piperidine is thus, contrary to Dickinson's contention (*loc. cit.*), identical with that of hydrogen chloride in inducing activation of the methylene *group in* benzyl methyl ketone *in preference to the* methyl radical. A similar and equally unexpected reaction has recently been recorded by Lovett and Roberts (J., 1928, 1975) in the case of ω-phenylacetylacetophenone and salicylaldehyde, whereby the *methylene next to the phenyl group is activated.*

As a direct consequence of the above proof, it follows that the ketone (A) must be represented by formula (VII) and hence (B) must have some other constitution. This compound (m. p. 145°) has *again been investigated in greater detail, and it has been found*, as shown in the following table, that analytical values alone are insufficient evidence of structure.

	Aldehyde +	Ketone	− Water.	Mol. formula.	Mol. wt.	% C.	% H.	% OMe.
(*a*)	1 mol.	1 mol.	1 mol.	$C_{17}H_{16}O_2$	252	80·9	6·4	12·3
(*b*)	2 mols.	1 mol.	2 mols.	$C_{25}H_{22}O_3$	370	81·1	5·95	16·8
(*c*)	1 mol.	2 mols.	1 mol.	$C_{26}H_{26}O_3$	386	80·8	6·7	8·0

Recourse has now been made to the determination of both molecular weight and methoxyl content, and satisfactory proof provided that (B) has actually been formed according to reaction (*b*). It is doubtful, however, whether substance (B) is the normal distyryl ketone (X), as an isomeric *compound*, m. p. 180°, has been obtained by direct condensation, by means of hydrogen chloride, of th aldehyde and the ketone in the requisite molecular proportion These two compounds may be stereoisomerides, or one of then (probably B) may have a *cyclo*pentenone structure such as (XI) (compare Japp and Maitland, J., 1904, **85**, 1473).

(XI.) 

CHPh:CH·CO·CH(CHMe₂)·CO₂H

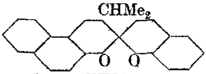
(XII.)

The application of the *spiro*pyran colour reaction has thus led to definite conclusions regarding the structure of these ketones.

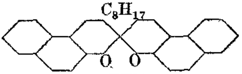
The rule that condensation involves the methyl group or the methylene group according as alkali or hydrogen chloride is used is not without exceptions. Stoermer and Wehln (*loc. cit.*) have shown that the condensation of benzaldehyde with phenoxyacetone invariably occurs at the methylene group. On the other hand, Gheorghiu and Arwentiew (*loc. cit.*) found that with methyl *iso*butyl ketone and benzaldehyde the use of either alkali or hydrogen chloride gave rise to styryl *iso*butyl ketone, the structure of which they proved by oxidation to benzoic and *iso*valeric acids. We have added the final proof by synthesising this compound from *iso*propylacetoacetic ester: by condensation with benzaldehyde in presence of alkali, *γ-benzylidene-α-*iso*propylacetoacetic acid* (XII) was obtained (compare Ryan and Shannon, *Proc. Roy. Irish Acad.*, 1924, **36**, B, 322); this, on being heated with copper powder, readily gave styryl *iso*butyl ketone, the semicarbazone of which gave no depression in melting point when mixed with that obtained from the alkali condensation product.

We have also been able to confirm the changes in colour of the semicarbazone under the influence of light noted by Gheorghiu and Arwentiew (*loc. cit.*). This case adds a further interesting example to the phenomenon of "reversed phototropy" originally observed by Heilbron and Wilson (J., 1914, **105**, 2892).

Methyl *iso*butyl ketone has now been condensed with salicylaldehyde in presence of alkali, and the resultant *2-hydroxystyryl* iso*butyl ketone* converted into *3′-*iso*propylbenzo-β-naphtha*spiro*pyran* (XIII), this structure being confirmed by the inability of the compound to acquire colour in high-boiling solvents. The same *spiro*pyran has been obtained by the condensation of salicylaldehyde



(XIII.)



(XIV.)

with methyl *iso*butyl ketone in presence of hydrogen chloride, followed by the condensation of the pyrylium salt with 2-naphthol-1-aldehyde and subsequent hydrolysis. This reaction affords independent proof that methyl *iso*butyl ketone condenses with aldehydes at the methyl radical whether acid or alkali is used as catalyst.

*3′-Octylbenzo-β-naphtha*spiro*pyran* has been prepared from 2-hydroxystyryl nonyl ketone (Heilbron and Irving, J., 1928, 2323) and in conformity with the general rule fails to show colour development. On the other hand, *3-octyldi-β-naphtha*spiro*pyran* (XIV) reacts normally, giving a purple colour in xylene.

The *preparation of benzo-β-naphthaspiropyrans* by first condensing the ketone with salicylaldehyde by means of hydrogen chloride and then adding 2-naphthol-1-aldehyde to the solution of the pyrylium salt is usually difficult. Frequently the corresponding di-β-naphtha*spiro*pyran alone is isolated; probably the salicylaldehyde forms in the first place the 2-hydroxystyrylbenzopyrylium salt, leaving half the ketone free to react with the other aldehyde. The use of low temperature (−5° or −10°) in carrying out the first stage is beneficial.

We have failed to find any relation between the readiness with which the *spiro*pyrans are transformed to pyrylium salts and the development of the colour change as suggested by Dilthey and Wübken (*Ber.*, 1928, **61**, 963; compare also Dickinson, Heilbron, and O'Brien, J., 1928, 2077). Whereas (XIII) fails to give evidence of ion formation even in boiling diphenyl ether, 3-*isopropyldi-β-naphtha*spiro*pyran* gives a purple solution in boiling xylene. Both substances, however, give marked pyrylium salt colorations in glacial acetic acid.

E X P E R I M E N T A L.

*3-Phenylbenzo-β-naphtha*spiro*pyran* (IX).—(1) A solution of 2-hydroxy-α-phenylstyryl methyl ketone (compound A, 1·5 g.) and 2-naphthol-1-aldehyde (1 g.) in absolute alcohol (15 c.c.) was saturated with dry hydrogen chloride. After a short time, the separated pyrylium salt was dissolved in aqueous acetone and hydrolysed with the minimum amount of dilute ammonia solution giving the *spiro*pyran, which was recrystallised from acetone anc then from benzene.

(2) A cold solution of salicylaldehyde (2 g.) and benzyl methy ketone (2·2 g.) in absolute alcohol (5 c.c.) was slowly saturated wit dry hydrogen chloride. The mixture was kept at 0° for a fe hours, and a solution of 2-naphthol-1-aldehyde (3 g.) in absolut alcohol (10 c.c.) then added. More hydrogen chloride was passe in and after standing in the cold for a few hours the separate pyrylium salt was treated in the manner described above.

The pure spiro*pyran* forms colourless crystals melting at 208- 209° to a purple liquid which loses its colour on cooling. A colou less solution of the compound in cold xylene becomes faintly colour on heating. A more pronounced colour change is visible in high boiling solvents; in nitrobenzene, for example, a strong reddis blue colour is produced (Found: C, 86·5; H, 5·0. $C_{27}H_{18}O_2$ requi C, 86·6; H, 4·8%). The isomeric 3'-phenylbenzo-β-naptha*spi* pyran has m. p. 147—148° (Dilthey, Berres, Hölterhoff, and Wübk *loc. cit.*).

Compound B (m. p. 145°).—This compound was prepared acco

ing to Dickinson's method (*loc. cit.*). The product failed to decolorise a solution of bromine in chloroform, and dissolved in concentrated sulphuric acid to give a yellow solution which darkened slightly on long standing [Found: C, 81·05, 81·0; H, 6·0, 6·0; MeO, 15·4; *M* (Menzies), 387, 378, 390. $C_{25}H_{22}O_3$ requires C, 81·1; H, 5·95; MeO, 16·8%; *M*, 370].

The Isomeric Compound, m. p. 180° (X ?).—A solution of *o*-methoxybenzaldehyde (5 g.) and benzyl methyl ketone (2·5 g.) in absolute alcohol (40 c.c.) was slowly saturated with dry hydrogen chloride at −5°. After standing for 4 hours at 0°, the solution was poured into water and neutralised with sodium carbonate, and the product extracted with ether. The ethereal solution was dried and the residue, after removal of solvent, taken up in hot alcohol. The crude *ketone* which separated on cooling was recrystallised from ethyl acetate, giving pale yellow rhombs, m. p. 180°, which dissolved in concentrated sulphuric acid to a cherry-red solution (Found: C, 80·7; H, 5·9; MeO, 16·5. $C_{25}H_{22}O_3$ requires C, 81·1; H, 5·95; MeO, 16·8%).

*γ-Benzylidene-α-*iso*propylacetoacetic Acid* (XII).—A suspension of benzaldehyde (7 g.) and *iso*propylacetoacetic ester (10 g.) in water (200 c.c.) was shaken for 11 days and during this period six portions (each of 5 c.c.) of 8% sodium hydroxide solution were added. Unchanged material was then removed by means of ether, and the aqueous portion acidified with acetic acid. The pure *acid* separated from dilute alcohol in colourless crystals, m. p. 134° (decomp.), readily soluble in the usual organic solvents (Found: C, 72·6; H, 7·1; *M*, 245. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%; *M*, 232).

Styryl iso*Butyl Ketone Semicarbazone*.—γ-Benzylidene-α-*iso*-propylacetoacetic acid (2 g.) was heated in presence of copper powder at 130—140° for 1½ hours. The oil obtained was dissolved in alcohol, and the semicarbazone prepared directly from the solution in the usual manner. After recrystallisation from alcohol, the pure substance melted at 167° and was found by means of a mixed m. p. determination to be identical with the semicarbazone obtained by Gheorghiu and Arwentiew (*loc. cit.*).

2-Hydroxystyryl iso*Butyl Ketone*.—To a solution of salicylaldehyde (12·2 g.) and methyl *iso*butyl ketone (10 g.) in alcohol (100 c.c.), sodium hydroxide (60 c.c. of 20% solution) was added. After 5 days, the dark red solution was nearly neutralised with acetic acid and diluted with an equal volume of water, and the product precipitated with carbon dioxide. The *ketone* crystallised from methyl alcohol (with freezing) in yellow rhombs, m. p. 104° (Found: C, 76·3; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

3′-iso*Propylbenzo-β-naphthaspiropyran* (XIII).—(1) A solution

of 2-hydroxystyryl *iso*butyl ketone (2 g.) and 2-naphthol-1-aldehyde (1·7 g.) in absolute alcohol (17 c.c.) was slowly saturated with dry hydrogen chloride and kept at 0° for 1 day. The pyrylium salt obtained was treated with dilute ammonia solution in presence of ether until the colour was discharged. The dry ethereal solution was evaporated, and the *spiro*pyran obtained from the oily residue by freezing and scratching in presence of a small quantity of acetone and methyl alcohol. Recrystallisation from a mixture of equal volumes of these solvents gave faintly yellow rhombs, m. p. 118°.

(2) A solution of salicylaldehyde (1 g.) and methyl *iso*butyl ketone (0·8 g.) in absolute alcohol (4 c.c.) was slowly saturated with dry hydrogen chloride at —10°. The mixture was kept at 0° for 15 hours to allow the primary condensation to reach completion; a solution of 2-naphthol-1-aldehyde (1·7 g.) in alcohol was then added and the whole again saturated with hydrogen chloride. The pyrylium salt, which separated after standing in the cold for 24 hours, was treated as described under (1), the same spiro*pyran* being obtained. The compound gave colourless solutions in boiling veratrole and diphenyl ether and dissolved in glacial acetic acid to a deep red solution (Found: C, 84·6; H, 6·2. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

3-iso*Propyldi-β-naphtha*spiro*pyran*.—A solution of 2-naphthol-1-aldehyde (3·4 g.) and methyl *iso*butyl ketone in absolute alcohol (30 c.c.) was saturated with a slow stream of dry hydrogen chloride. The deep blue solution was kept over-night at 0° and the separated pyrylium salt was then dissolved in aqueous acetone and treated with sufficient dilute ammonia solution to discharge the colour. The product on recrystallisation from benzene formed colourless prisms which melted to a purple liquid at 204° (Found: C, 86·0; H, 5·9. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·6%). Solutions in cold xylene or veratrole are colourless, but become purple at the boiling point. The spiro*pyran* dissolves in glacial acetic acid, forming a blue solution of the pyrylium salt.

3′-*Octylbenzo-β-naphtha*spiro*pyran*.—A solution of 2-hydroxystyryl nonyl ketone (1·5 g.) and 2-naphthol-1-aldehyde (1 g.) in absolute alcohol (15 c.c.) was saturated with dry hydrogen chloride and maintained at 0° for 2 days. The pyrylium salt which had then separated was suspended in ether and treated with sufficient dilute ammonia solution to remove the colour. The ethereal layer was evaporated and the product recrystallised from aqueous acetone, colourless needles being obtained, m. p. 101—102°. Solutions of the compound in boiling xylene or boiling diphenyl ether remained colourless (Found: C, 84·8; H, 7·2. $C_{29}H_{30}O_2$ requires C, 84·9; H, 7·3%).

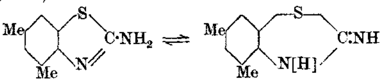
3-*Octyldi-β-naphtha*spiro*pyran* (XIV).—A solution of methyl nonyl ketone (1 g.) and 2-naphthol-1-aldehyde (2 g.) in absolute alcohol (15 c.c.) was saturated with dry hydrogen chloride and kept at 0° for 2 days. The separated pyrylium salt was dissolved in aqueous acetone, and the solution treated with sufficient dilute aqueous ammonia to effect hydrolysis. The *product* was recrystallised from benzene, giving colourless needles, m. p. 157° (Found : C, 85·9; H, 7·2. $C_{33}H_{32}O_2$ requires C, 86·1; H, 7·0%). Its solution in xylene was colourless in the cold, but became purple on boiling; the colour disappeared when the solution was cooled.

THE UNIVERSITY, LIVERPOOL. [*Received, March 9th,* 1929.]

CXXV.—*Aminobenzthiazoles. Part XII. The Mobility of 1-Amino-3 : 5-dimethylbenzthiazole. A Case of Complete Reactivity in the Aminothiazole Form.*

By ROBERT FERGUS HUNTER and WILLIAM EMRYS PRIDE.

THE symmetrical triad system in 1-amino-3 : 5-dimethylbenzthiazole responded satisfactorily to the symmetry test of mobility, since the hydrolysis of 1-*imino-2-acetyl-3 : 5-dimethyl-1 : 2-dihydrobenzthiazole* and of 1-*acetamido-3 : 5-dimethylbenzthiazole* yielded the same base (I ⇌ II) (compare Hunter, J., 1926, 1385; Hunter and Styles, J., 1928, 3019).

(I.)  (II.)

On the other hand, the methylation of this single individual with methyl iodide under mild, and also under vigorous, conditions yielded exclusively the *hydriodide* of 1-imino-2 : 3 : 5-trimethyl-1 : 2-dihydrobenzthiazole, no trace of the hydriodide of the isomeric 1-methylamino-base being obtained.

Attempts to isolate intermediate products in these methylations were unsuccessful. When 1-amino-3 : 5-dimethylbenzthiazole was treated with methyl sulphate in benzene, however, a *methosulphate* was obtained which was decomposed by strong alkalis with regeneration of the amino-base.

EXPERIMENTAL.

m-Xylylthiocarbimide, b. p. 262—263°/760 mm. (corr.), was prepared in 95% yield from *s*-di-*m*-xylylthiocarbamide (m. p. 152—153°; Dyson and George, J., 1924, 125, 1705, give 149—150°).

by the method used in the case of the *o*-tolyl compound (Hunter and Styles, *loc. cit.*).

1-Amino-3 : 5-dimethylbenzthiazole was prepared by reduction of the bromo-addition compound obtained from *m*-xylylthiocarbamide (0·7 c.c. of bromine and 6 c.c. of chloroform to 1 g. of the thiocarbamide), suspended in sulphurous acid, with sulphur dioxide. The base separated from 50% alcohol in needles, m. p. 139—140°. The lower m. p. originally assigned to this base (J., 1926, 1400) was due to a trace of solvent, which is removed by drying at 100°. The intermediate bromo-addition *compound*, which is usually very unstable, was isolated by using dried materials; it formed orange needles, m. p. 273° (decomp.) (Found: Br, 46·9. $C_9H_{10}N_2Br_2S$ requires Br, 47·3%).

Synthesis of 1-*Amino*-3 : 5-*dimethylbenzthiazole from* 1-*Imino*-2-*acetyl*-3 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole and from* 1-*Acetamido*-3 : 5-*dimethylbenzthiazole*.—Labile *acetyl*-m-*xylylthiocarbamide* was prepared from 5 g. of *m*-xylylthiocarbamide and 11 c.c. of acetic anhydride at 75° (compare Hugershoff, *Ber.*, 1899, **32**, 3649) in short needles, m. p. 121—122° (Found: S, 14·6. $C_{11}H_{14}ON_2S$ requires S, 14·4%). Difficulty was frequently experienced in obtaining it, owing to the ease with which it passed into the stable isomeride, the change being catalysed by acetic anhydride.

1-*Imino*-2-*acetyl*-3 : 5-*dimethyl*-1 : 2-*dihydrobenzthiazole* was pre pared in the same manner as the *o*-tolyl homologue (Hunter anc Styles, *loc. cit.*), and separated from dilute alcohol in small granules m. p. 118° (Found: S, 14·1. $C_{11}H_{12}ON_2S$ requires S, 14·5%). I was recovered unchanged after being heated under reflux with 60% sulphuric acid for 3 hours, but yielded the aminobenzthiazole whe heated with 30% hydrochloric acid for 4 hours. Stable *acety* m-*xylylthiocarbamide* crystallised from alcohol in long prisms, m.] 181—182° (Found: S, 14·7%).

1-*Acetamido*-3 : 5-*dimethylbenzthiazole hydrotribromide*, obtaine by treating a suspension of 1·5 g. of stable acetyl-*m*-xylylthiocar amide in chloroform (10 c.c.) with bromine (1·1 c.c. in 3 c.c. chloroform) and heating the mixture under reflux for a few minut crystallised in orange needles, m. p. 167° (decomp.) (Found: Br, 52 $C_{11}H_{13}ON_2Br_3S$ requires Br, 52·1%). The *acetamidobenzthiazc* obtained by reduction with sulphurous acid, separated from alcoh ...hyl acetate in plates, m. p. 259—260° (Found: S, 14·7%), and v ...ntical with the product obtained by heating a solution of 1-ami ... dimethylbenzthiazole (8 g.) in acetic anhydride (33 c.c.) a ... (100 c.c.).

...*ation of* 1-*Amino*-3 : 5-*dimethylbenzthiazole*.—(A) A mixt ...mino base (8 g.) and methyl iodide (9 c.c.) was heated

th dilu was ev colourle the comp colourless H, 7·3%).

100° for 24 hours and the product was finely ground and extracted with 250 c.c. of boiling alcohol. The residue (11·5 g.) consisted of the hydriodide of the iminomethyl base, m. p. 265° (decomp.), and was identical with the product of methylation in benzene. Fractional crystallisation of the alcoholic extract yielded a hydriodide (1 g.) and 1·1 g. of a dark-coloured solid, m. p. 185—190°.

The insoluble hydriodide was decomposed by heating with 30% sodium hydroxide solution for an hour; the base, which was isolated by extraction with ether or chloroform, formed a clear tenacious gum which sometimes solidified on keeping in a vacuum. On recrystallisation from 70% methyl alcohol, 1-*imino*-2 : 3 : 5-*trimethyl*-1 : 2-*dihydrobenzthiazole* was obtained in small colourless crystals, m. p. 105—106° (Found : S, 16·9. $C_{10}H_{12}N_2S$ requires S, 16·7%). On treatment with acetic anhydride, the gum gave an almost quantitative yield of the *acetyl* derivative, which crystallised from alcohol–ethyl acetate in plates, m. p. 186° (Found : N, 12·3; S, 13·9. $C_{12}H_{14}ON_2S$ requires N, 12·0; S, 13·7%). The *hydriodide* obtained from the iminomethyl base and hydriodic acid was identical with that obtained in the methylation: on recrystallisation from alcohol (animal charcoal), it formed soft plates having a silvery-green lustre, m. p. 274° (decomp.) [Found: C, 37·7; H, 3·9 (Pregl's method); I, 39·6; S, 9·7. $C_{10}H_{12}N_2S$, HI requires C, 37·5; H, 4·1; I, 39·7; S, 10·0%].

The hydriodide and the dark-coloured product, m. p. 185—190°, obtained by fractional crystallisation of the alcoholic extract, when decomposed in the same way, did not yield any trace of the methylamino-derivative; the latter yielded some unchanged 1-amino-3 : 5-dimethylbenzthiazole (identified as the acetyl derivative).

In attempts to isolate the intermediate methiodide through which methylation is assumed to take place (Hunter and Styles, *loc. cit.*), either the original materials were recovered unchanged, or the iminomethylbenzthiazole derivative was formed.

(B) The quantity of material methylated in benzene solution was inappreciable in the first few hours; the following experiment is typical of a number. A mixture of 10 g. of 1-amino-3 : 5-dimethylbenzthiazole, methyliodide (20 c.c.), and benzene (30 c.c.) was heated under reflux for 16 hours. The hydriodide (2·3 g.; m. p. 266°) separated in the later stages. On fractional crystallisation, the mother-liquor yielded unchanged 1-amino-3 : 5-dimethylbenzthiazole, and an iodine-free *substance* which crystallised in needles, m. p. 156—157° (Found by Pregl's method: C, 62·2; H, 6·0%), and has not yet been identified.

1-*Methylamino*-3 : 5-*dimethylbenzthiazole and its Derivatives*.—s-m-*Xylylmethylthiocarbamide*, prepared from *m*-xylylthiocarbimide

(6 g.) in alcohol, and methylamine (30% excess), crystallised in plates, m. p. 152° (Found: S, 16·6. $C_{10}H_{14}N_2S$ requires S, 16·5%). 1-*Methylamino*-3 : 5-*dimethylbenzthiazole* was prepared by reducing the orange bromo-addition compound (m. p. 129°) obtained from the methylthiocarbamide (4 g.), chloroform (20 c.c.), and bromine (3·5 c.c.); it separated from alcohol in needles, m. p. 124—125° (Found: S, 16·8%). The *acetyl* derivative crystallised from alcohol–ethyl acetate in needles, m. p. 156—157° (Found: S, 13·7%). The *hydriodide*, which was much more soluble in ordinary solvents than the iminomethyl isomeride, crystallised from alcohol in needles, m. p. 225—227° (decomp.) (Found: I, 39·3%).

1-*Amino*-3 : 5-*dimethylbenzthiazole methosulphate* was prepared by heating a solution of the aminothiazole (5 g.) in benzene (25 c.c.) and methyl sulphate (10 c.c.) under reflux for 3 hours; it separated from methyl alcohol in colourless needles, m. p. 216—217° (Found: S, 20·8. $C_{11}H_{16}O_4N_2S_2$ requires S, 21·05%). Decomposition of 0·8 g. of this compound with 20% potassium hydroxide solution yielded 0·35 g. of 1-amino-3 : 5-dimethylbenzthiazole (m. p. 137—138° after recrystallisation).

The authors wish to express their gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in this work, to the Trustees of the Ramsay Memorial Fellowship Trust for the award of a Fellowship to one of them (R. F. H.), and also to the Trustees of the Dixon Fund of the University of London for grants which have defrayed the cost of the materials.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CXXVI.—*The Isomerism of the Oximes. Part XXXIV. The Dissociation Constants of Isomeric Oximes and their Influence on the Production of the Isomerides in Alkaline Solution.*

By OSCAR L. BRADY and NAVNITLAL MOHANLAL CHOKSHI.

THE results of the determination of the dissociation constants of a number of aldoximes (Brady and Goldstein, J., 1926, 1923) showed that in the case of substituted benzaldoximes, where only the oow oxime was produced when oximation was carried out in alkaline the c.. the α- was about four times as strong an acid as the β-iso-colourl..., that α-cinnamaldoxime was only about twice as strong
H. 7·34min

an acid as β-cinnamaldoxime. In the latter case oximation in alkaline solution yields both the α- and the β-oxime.

This suggested that when an aldehyde or unsymmetrical ketone was treated with an alkaline solution of hydroxylamine the configuration of the resulting oxime bore some relation to the dissociation constants of the two possible isomerides. That is, if the dissociation constants were widely different, only the oxime with the higher constant would be obtained, but if they were nearly the same both isomeric oximes would be formed. Further work bears out this hypothesis : the results are shown in Table I, where the dissociation constants of eight pairs of isomeric oximes are given.

TABLE I.

	$K_a \times 10^{11}$.	$K_a\alpha/K_a\beta$.
α-Benzaldoxime	2·1	4·5 : 1
β- ,,	0·47	
α-*o*-Nitrobenzaldoxime	8·7	4·8 : 1
β- ,,	1·8	
α-*m*-Nitrobenzaldoxime	7·0	3·9 : 1
β- ,,	1·8	
α-Cinnamaldoxime	2·8	2·1 : 1
β- ,,	1·3	
α-*o*-Methoxycinnamaldoxime	1·6	3·5 : 1
β- ,,	0·45	
α-Furfuraldoxime	1·5	1·1 : 1
β- ,,	1·4	
α-*p*-Nitrobenzophenoneoxime	1·4	1 : 2·4
β- ,,	3·4	
α-Phenyl-*p*-tolylketoxime	—	1·4 : 1 *
β- ,,	—	

* Deduced from quantitative methylation experiments.

o-Methoxycinnamaldehyde, unlike cinnamaldehyde, gives little if any of the β-oxime with hydroxylamine in alkaline solution, behaving more like the substituted benzaldoximes (Brady and Grayson, J., 1924, 125, 1418), and it is found that the ratio $K_a\alpha/K_a\beta$ approaches that of the *m*-nitrobenzaldoximes. Furfuraldehyde, on the other hand, on oximation under these conditions readily gives an inseparable mixture of the α- and β-isomerides (Brady and Goldstein, J., 1927, 1959). Although we have no quantitative figures, qualitative experience shows that more of the β-isomeride is produced in this case than in that of cinnamaldehyde, as would be expected from the lower $K_a\alpha/K_a\beta$ ratio.

The α- and β-*p*-nitrobenzophenoneoximes do not differ greatly in their dissociation constants. Here the oxime to which the label β has been attached happens to be the stronger acid, but this has no real significance, since the α- and β-titles have not, in the ketoximes, the special connotation they bear in the aldoximes (Brady and Bishop, J., 1925, 127, 1361). Similarly, the α- and β-phenyl-

p-tolylketoximes are both acids of about the same strength; direct measurement of the dissociation constants in this case has been found impracticable for reasons given in the experimental part, but some idea of the relative strengths of the two acids can be gained from a quantitative study of their methylation : this will be the subject of a later paper (compare Brady and Goldstein, J., 1926, 2403). *p*-Nitrobenzophenone and phenyl *p*-tolyl ketone on oximation in alkaline solution both give a mixture of the α- and the β-ketoxime (Brady and Mehta, J., 1924, **125**, 2298; Hantzsch, *Ber.*, 1890, **23**, 2325).

Brady and Goldstein (J., 1926, 1918) showed that if the new configurations for the benzaldoximes are accepted the relation between configuration and dissociation constant in these compounds is not analogous to that in the cinnamic acids, since the stronger acid is that in which the phenyl group is remote from the hydroxyl group. The dissociation constants of the two forms of *p*-nitrobenzophenone-oxime and phenyl-*p*-tolylketoxime bear this out, since, if the new configurations are adopted, the stronger acid has in the first case the *p*-nitrophenyl and in the second the phenyl group remote from the hydroxyl. The new configurations of the ketoximes rest on more experimental evidence than those of the aldoximes and either this evidence is also unsound or the analogy with *cis*- and *trans*-acids in the ethylene series will not hold. Since there is between the two acidic groups a chain of two atoms in the oximes and of three in ethylene compounds ($C_6H_5{\cdot}C{=}N{-}OH$, $C_6H_5{\cdot}C{=}C{-}C{-}OH$), the comparison may not be a fair one.

On the above lines it is possible to suggest an explanation of the apparent exclusive formation of β-aldoximes when aliphatic aldehydes are oximated. For example, in benzaldoxime the phenyl group has a greater electron affinity than the methine hydrogen atom; the effect of this is so transmitted that the hydrogen of the hydroxyl group is more easily expelled as an ion when the hydroxyl group is remote from the phenyl group, that is, the α-oxime is the stronger acid and is formed on oximation in alkaline solution. Now in the aliphatic aldoximes the methine hydrogen atom has a greater electron affinity than the alkyl group and consequently the stronger acid will be that in which the hydroxyl is remote from the methine hydrogen, namely, the β-oxime, which will consequently be formed on oximation. The lack of a suitable method of converting a stable β-aldoxime into the α-isomeride would explain the failure to obtain satisfactory evidence of the existence of the latter form among aliphatic aldoximes. Attempts to bring this change about through the benzoyl derivative, successful in the case of β-cinnamaldoxime (Brady and Grayson, *loc. cit.*), have so far yielded negative results.

Our conclusions have been drawn from a more limited number of examples than we could have desired, but owing to the very sparing solubility in water of most of the β-oximes and the ready hydrolysis of their sodium salts the determination of their dissociation constants presents unusual difficulties, and we have failed to obtain figures in other cases we have tried. Measurements of hydrogen-ion concentration with the glass electrode were unsuccessful owing to progressive hydrolysis of the oxime to aldehyde and hydroxylamine in the very dilute aqueous solutions that had of necessity to be employed. We are indebted to Mr. B. Prasad for investigating this method.

The dissociation constants of α-*p*-dimethylaminobenzaldoxime ($K_a = 0{\cdot}56 \times 10^{-11}$), acetophenoneoxime ($K_a = 0{\cdot}33 \times 10^{-11}$), and benzophenoneoxime ($K_a = 0{\cdot}50 \times 10^{-11}$) have also been measured.

EXPERIMENTAL.

The conductivity method previously employed (Brady and Goldstein, *loc. cit.*) for the measurement of the dissociation constants of some aldoximes cannot be used for those oximes which are very weak acids and sparingly soluble in water owing to the separation of the solid oxime when the sodium salt dissociates hydrolytically. For this reason the method of Farmer (J., 1901, **79**, 863), depending upon the measurement of the degree of hydrolysis of the sodium salt as determined by the distribution coefficient of the oxime between aqueous sodium hydroxide and an organic solvent, has been employed. Even this method is not applicable to such weak acids as phenyl-*p*-tolylketoxime, as, owing to the very large proportion of the oxime that passes into the organic solvent, concordant results cannot be obtained.

In the following experiments, water and sodium hydroxide free from carbon dioxide were employed, the solutions were preserved in waxed bottles, and the usual precautions observed to prevent access of carbon dioxide during manipulation. The temperature throughout was 25° ± 0·04°. The mutual solubilities of water and benzene were taken as 100 c.c. of water dissolve 0·082 c.c. of benzene and 100 c.c. of benzene dissolve 0·211 c.c. of water.

In order to determine the distribution coefficient of the oxime between water and benzene, a weighed amount of oxime, insufficient to saturate the solvents, was shaken with a mixture of known amounts of benzene and water for 6 hours at constant temperature and the solutions were left in the thermostat to separate. Three portions of 10 c.c. were pipetted from the benzene layer and the oxime therein was determined either by evaporation on the water-bath and drying at 100° to constant weight or, with the more

volatile oximes, by evaporation in a current of dry air at room temperature and drying in a vacuum to constant weight. The aqueous layer was examined in either of two ways. A quantity (100—400 c.c. depending on the solubility of the oxime) was extracted several times with chloroform, and the oxime determined by evaporation as before. Alternatively, 100—500 c.c. were acidified with hydrochloric acid (25 c.c. of concentrated acid for each 100 c.c. of solution), a solution of 2 : 4-dinitrophenylhydrazine hydrochloride was added, and the mixture warmed and kept over-night. The very sparingly soluble dinitrophenylhydrazone was collected, dried at 100°, and weighed (compare Brady and Elsmie, *Analyst*, 1926, 77). In the case of oximes which did not give concordant results by this method owing to their very small solubility in water, the solubilities in water saturated with benzene and in benzene saturated with water were determined separately (compare Farmer, *loc. cit.*) and their ratio was taken as the distribution coefficient.

The degree of hydrolysis of the sodium salt was measured by shaking a weighed quantity of oxime with known amounts of benzene, water, and sodium hydroxide solution for 6 hours in a thermostat and then allowing the two layers to separate. The oxime in the benzene layer was determined as before. The results were calculated from the equations (Farmer, *loc. cit.*)

$$K = \frac{c[c_1 - c_2 + c(1 + qF)]}{c_2 - c(1 + qF)}, \quad m_1 = \frac{\sqrt{K^2 + 4Kc_2} - K}{2}$$

$$x = m_1/c_2, \quad K_h = x^2/(1 - x)v, \quad K_a = K_w/K_h,$$

where c = concentration of free oxime in the aqueous layer after

TABLE II.

		Vol. of water.	Vol. of benzene.	F.	$c_1 \times 10^4$.	$c_2 \times 10^4$.	G. of oxime in 20 c.c. of benzene layer.	$K_a \times 10^{11}$.
α-*o*-Methoxybenzaldoxime	(1)	500	50	60·30	14·32	14·12	0·2225	1·45
	(2)	500	50	60·30	17·05	13·69	0·1689	1·60
α-*m*-Nitrobenzaldoxime	(1)	270	50	24·00	10·20	9·20	0·0604	7·10
	(2)	500	100	24·00	17·05	14·62	0·0424	6·09
α-*p*-Nitrobenzaldoxime		500	50	18·05	18·84	17·88	0·0478	10·93
α-*p*-Dimethylaminobenzaldoxime	(1)	517	75	46·72	12·41	12·37	0·2472	0·55
	(2)	275	50	46·72	18·30	13·23	0·2466	0·57
α-Furfuraldoxime	(1)	276	50	1·01	18·92	18·92	0·0186	1·46
	(2)	125	50	1·01	18·30	17·34	0·0140	1·33
β-Furfuraldoxime	(1)	113	50	2·51	9·26	9·26	0·0284	1·57
	(2)	114	100	2·51	13·83	13·83	0·0262	1·43
α-*o*-Methoxycinnamaldoxime	(1)	250	50	162·0	7·19	6·16	0·2294	1·61
	(2)	500	50	162·0	10·79	7·25	0·2196	1·56
β-*o*-Methoxycinnamaldoxime	(1)	500	50	147·0	7·19	5·02	0·2520	0·45
	(2)	500	50	147·0	10·14	6·50	0·2072	0·44
α-*p*-Nitrobenzophenoneoxime	(1)	257	50	1072·0	5·27	5·02	0·4370	1·21
	(2)	520	50	1072·0	14·78	5·72	0·3972	1·59
β-*p*-Nitrobenzophenoneoxime		500	50	1943·0	7·19	6·35	0·2529	3·37
Benzophenoneoxime	(1)	500	50	1183·0	40·62	5·52	0·3291	0·48
	(2)	500	75	1183·0	13·58	4·88	0·2318	0·53
Acetophenoneoxime	(1)	500	50*	7·62	14·93	14·86	0·1258	0·33
	(2)	116	50*	7·62	11·71	11·35	0·1898	0·53

* Light petroleum (b. p. 60—80°) was used in place of benzene.

shaking with benzene, c_1 = concentration of sodium hydroxide in mols., c_2 = concentration of oxime in mols., q = ratio of volume of benzene layer to sodium hydroxide layer, F = distribution coefficient of oxime between benzene and pure water, m_1 = concentration of free oxime in the aqueous layer, x = degree of hydrolysis of the sodium salt of the oxime, K_h = hydrolysis constant, v = number of litres of water containing a gram-molecule of oxime, K_w = ionic constant of water = $1{\cdot}00 \times 10^{-14}$, K_a = dissociation constant of oxime. The observed figures are given in Table II.

The dissociation constants of *m*- and *p*-nitrobenzaldoximes and of *o*-methoxybenzaldoxime were determined by this method to test its applicability. The mean results, 6·9, 10·9, $1{\cdot}5 \times 10^{-11}$, respectively, agree satisfactorily with those determined by conductivity methods, 7·0, 10·7, $1{\cdot}3 \times 10^{-11}$ (Brady and Goldstein, *loc. cit.*).

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 4th*, 1929.]

CXXVII.—*Compounds of Hydroxides of the Alkaline Earths with Sugars.*

By JOHN EDWIN MACKENZIE and JAMES PATTERSON QUIN.

IN 1807, William Ramsay (*Nicholson's Journal*, **18**, 9) described experiments from which he concluded that sucrose, in aqueous solution at 50° F., dissolved half its weight of lime and an equal weight of strontia. From the latter solution, grey crystals separated, but no analytical data are given by Ramsay for what was in all probability monostrontia-monosucrose.

Peligot (*Compt. rend.*, 1838, **6**, 232) prepared and analysed a number of compounds of sucrose and "earths." The results recorded in numerous subsequent papers are so discordant that it seemed desirable to obtain exact data concerning these compounds and to distinguish between true compounds and intimate mechanical mixtures. In pursuance of this object, one of us (J. E. M.) incidentally repeated the isolation of calcium carbonate hexahydrate (J., 1923, **123**, 2409) from a lime–sugar solution. Preliminary experiments by Messrs. John Hume and H. B. Walker gave valuable results and a full description of the subsequent work appears in the thesis submitted by J. P. Quin to the University of Edinburgh.

Some of the names applied to these compounds are unsuitable, *e.g.*, "saccharate" (Peligot, *loc. cit.*), "sucrate" and "lactate" (Horsin-Déon, *Bull. Soc. chim.*, 1871, **16**, 26). Until more knowledge of the structure has been gained, the nomenclature of Soubeiran

(*J. Pharm. Chim.*, 1842, **1**, 469), in which the name of the alkaline earth and of the sugar are combined, will be used.

As many as seven lime-sucrose compounds have been described, but, as will be shown, the existence of more than three is very improbable.

Monolime-monosucrose (Peligot, *Compt. rend.*, 1864, **59**, 930; Benedikt, *Ber.*, 1873, **6**, 413; Stromeyer, *Arch. Pharm.*, 1887, **25**, 229) exists as an unstable hexahydrate, $C_{12}H_{22}O_{11},CaO,6H_2O$. We found it difficult to isolate this hydrate and, on triturating it with dilute alcohol, the lime content rose until it reached that required for dilime-monosucrose.

Brendeke (*Arch. Pharm.*, 1842, **29**, 73), Soubeiran (*loc. cit.*), and Stromeyer (*loc. cit.*) claim to have prepared trilime-disucrose. The product obtained by us on following the directions of these authors is probably a mixture of the unstable monolime-monosucrose with the more stable dilime-monosucrose, since on trituration with dilute alcohol it, like monolime-monosucrose, yields dilime-sucrose.

Dilime-monosucrose was first described by Pelouze (*Compt. rend.*, 1864, **59**, 1073). It is the final product obtained by washing with dilute alcohol the precipitate formed by adding alcohol to a sugar-lime solution. Peligot (*Compt. rend.*, 1864, **59**, 930) pointed out that the proportion of two molecules of lime to one of sugar is never attained in solution and that the precipitation by alcohol leaves a mother-liquor richer in sugar. Dilime-monosucrose is a comparatively stable substance.

Trilime-monosucrose ($C_{12}H_{22}O_{11},3CaO,4H_2O$) was obtained by Seyffart (*N.Z. Rübenzuckerind.*, **3**, 178) by the action of three molecular proportions of lime on an alcoholic solution containing one molecular proportion of sucrose. Soubeiran (*loc. cit.*), Wachtel (*O.Z. Zuckerind.*, **7**, 704; **8**, 860) and Lippmann (*ibid.*, **9**, 95) all claim to have obtained $C_{12}H_{22}O_{11},3CaO,3H_2O$ by heating a sugar-lime solution. As mentioned below (p. 957), our product appears to be a hexahydrate. Horsin-Déon (*loc. cit.*) observed that precipitation of trilime-sucrose does not take place on heating to 100° a lime–sugar solution containing excess of sugar, but, if the density of the solution be lowered by the addition of water, precipitation does take place. In other words, trilime-sucrose is more soluble in an aqueous solution of sugar at low than at high temperatures and also more soluble in a highly concentrated than in a less concentrated sugar solution.

Stulzer and Sostmann (*Z. Ver. deut. Zuckerind.*, 1884, **34**, 85) and Wolters (*N.Z. Rübenzuckerind.*, **10**, 287) claim to have prepared tetralime-monosucrose; Degener (*Z. Ver. deut. Zuckerind.*, 1884, **34**, 283) disclaims its existence. Soubeiran (*loc. cit.*) and

Horsin-Déon (*Bull. Soc. chim.*, 1872, **17**, 155) described the preparation of hexalime-monosucrose, but gave no analyses; Peligot (*Compt. rend.*, 1851, **32**, 333) denied its existence. Wolters (*loc. cit.*) affirmed the existence of octalime-monosucrose.

On heating sugar–lime solutions, unsaturated as regards lime, precipitates containing approximately the theoretical proportions of lime required for higher lime-monosucroses were obtained by us. These precipitates showed no trace of crystalline structure and on grinding with 90% alcohol, the lime content rose to 80% (see p. 958). It would appear that these so-called compounds are either sucrose, dilime- or trilime-sucrose adsorbed by lime.

Few physical data concerning sugar–lime compounds are available. Petit (*Compt. rend.*, 1893, **116**, 823) made a thermochemical investigation not only of the direct action of lime upon sucrose, but also of the interaction of sodium hydroxide with sucrose and calcium chloride in aqueous solution. His results may be summarised as follows :—

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11}} + \underset{\text{(solid)}}{Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},CaO} + 7\cdot2 \text{ Cal.}$$

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11}} + \underset{\text{(solid)}}{2Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},2CaO} + 11\cdot7 \text{ Cal.}$$

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},CaO} + \underset{\text{(solid)}}{Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},2CaO} + 4\cdot5 \text{ Cal.}$$

The addition of more calcium hydroxide was unaccompanied by further heat production and no trilime compound was formed in solution.

An accurate study of the solubility of lime in aqueous sugar solutions was made by Claassen (*Z. Ver. deut. Zuckerind.*, 1911, 489). Cameron and Patten (*J. Physical Chem.*, 1911, **15**, 67) found that on addition of lime to sucrose solution, not only was a soluble lime-sucrose compound formed, but some of the sucrose was removed from solution by the undissolved lime and passed into the solid phase. Dedek (*Z. Zuckerind. Czechoslov.*, 1925, **26**, 349) concluded from his potentiometric measurements that trilime-sucrose was not present in solution, and suggested that a colloidal adsorption compound was obtained by adding powdered calcium oxide to a sucrose solution or by heating lime-sucrose solution, which was saturated in the cold. Waterman and van Aken (*J. Soc. Chem. Ind.*, 1927, **46**, 411T) agree with Dedek's view of the nature of trilime-sucrose. Aten, van Ginneken, and Engelhard (*Rec. trav. chim.*, 1926, **45**, 753) found that in dilute alkaline solution (up to $0\cdot1N$) sucrose behaves as a monobasic acid with dissociation constant $14\cdot6 \times 10^{-14}$ at 18°. They also observed that little change in the metal-ion

concentration was produced by the addition of sucrose to alkaline solutions of less than normal concentration. Hence they concluded that the alkali-sucrose compounds in such solutions are largely ionised. Experiments made in this laboratory support this conclusion. In more concentrated solutions the low conductivities measured indicate the presence of undissociated molecules.

Diffusion experiments described below (pp. 958, 959, 960) proved that, *in aqueous solution*, the lime-sucrose, strontia-sucrose, and baryta-sucrose behave as crystalloids—diffusing readily.

Monostrontia-monosucrose was obtained in crystalline form by Ramsay (*loc. cit.*) and as pentahydrate by Scheibler (*N.Z. Rübenzuckerind.*, **9**, 83; **10**, 143). Our experiments show the compound to be a hexahydrate (p. 959).

Scheibler (*loc. cit.* and **6**, 49) claims to have prepared distrontia-trisucrose and distrontia-monosucrose and also tristrontia-monosucrose. Wolfmann (*Z. Ver. deut. Zuckerind.*, **52**, 587) showed that the last-named product is a mixture of distrontia-monosucrose and strontium hydroxide, a result confirmed by our experiments. Our attempts to prepare distrontia-trisucrose were unsuccessful (p. 959).

Monobaryta-monosucrose, $C_{12}H_{22}O_{11},BaO$, was first prepared by Peligot (*Annalen*, 1839, **30**, 69) and its composition has been confirmed by numerous investigators. Soubeiran (*Compt. rend.*, 1843, **14**, 648) claims also to have isolated dibaryta-monosucrose, but in our attempts to separate this compound the monobaryta compound has always been produced (p. 960).

Monolime-monoglucose was first described by Peligot (*Annalen*, 1839, **30**, 75) and the dihydrate by Soubeiran (*J. Pharm.*, 1842, **1**, 349). Though the instability of alkaline solutions of glucose is well known and has been the subject of very extensive investigations by Nef (*Annalen*, 1907, **357**, 294; 1910, **376**, 1) and others, anhydrous monolime-monoglucose is comparatively stable (p. 960). We have been unable to isolate any other compound than monolime-monoglucose.

Monolime-monofructose dihydrate was prepared by Peligot (*Compt. rend.*, 1880, **90**, 153) and the hexahydrate by Winter (*Annalen*, 1888, **244**, 295). Peligot (*J. Fabr. Sucre*, **21**, 6) claims to have prepared dilime-monofructose, but the resulting product in our experiments has always been monolime-monofructose.

Monolime-monomaltose was prepared by Herzfeld (*Annalen*, 1883, **220**, 214) and monolime-monolactose by Dubrunfaut (Lippmann, "Chemie der Zuckerarten," 1904). No other lime derivatives of either of these sugars appear to have been made.

From our experiments we conclude that the following definite

compounds can be prepared: monolime-monosucrose, dilime-monosucrose, trilime-monosucrose; monostrontia-monosucrose, distrontia-monosucrose; monobaryta-monosucrose; and monolime-monoglucose; monolime-monofructose; monolime-monomaltose; monolime-monolactose. It is further shown that the methyl-glucosides, -fructosides, -maltosides, and -lactosides are uninfluenced by calcium hydroxide. Our attempts to prepare compounds of reducing sugars with alkaline earths, other than those built up of one molecule of sugar and one molecule of earth, have not been successful.

The evidence at present on hand inclines us to suggest that in the compounds of the reducing sugars with lime the calcium is united to the "reducing" carbon group—possibly in the form $\cdot CH{<}^{O}_{O}{>}Ca$ or $:CH\cdot O\cdot Ca\cdot OH$; whereas in the non-reducing sugar, sucrose, the sucrose molecule attracts one, two or three molecules of lime, forming compounds comparable with those of sucrose with metallic salts, *e.g.*, $C_{12}H_{22}O_{11},KCl$ (Violette, *Compt. rend.*, 1873, **76**, 485).

In a future communication we hope to give an account of further experiments which will lead to a full discussion of the constitution of these substances.

Is it a coincidence that one molecule of sucrose can form a compound with three molecules of lime, with two molecules of strontia and with only one molecule of baryta? The molecular weights of these earths are: $3CaO = 168$; $2SrO = 207$; $BaO = 153\cdot 4$. The mean of the three is 176, which is approximately half of the molecular weight of sucrose—$342/2 = 171$.

EXPERIMENTAL.

The glass used in the following experiments had had lengthened contact successively with alkali, acid, conductivity water, sugar, and lime–sugar solutions. The apparatus for making lime–sugar solutions consisted of a bottle of 2 l. capacity, provided with a three-holed rubber stopper through which passed (*a*) a small funnel with ground glass stopper, (*b*) a soda–lime tube, (*c*) a glass tube in which rotated a stirrer reaching nearly to the bottom of the bottle. (*b*) allowed easy access of air free from carbon dioxide; whereas very little air entered through (*a*) while lime was being added and none entered through (*c*)—the space between the glass tube collar and the stirrer being filled with vaselin.

Lime was prepared from either Buxton limestone or precipitated calcium carbonate (Kahlbaum) by heating it for 6 hours in a muffle, grinding the product to a very fine powder, and reheating it for 4 hours. The lime produced did not effervesce when mixed with

dilute acid. In the sucrose experiments, so-called "Austrian crystals" were used, 100 g. being dissolved in conductivity water and the solution made up to 2000 c.c. Lime was added in small quantities at a time to the sucrose solution, which was vigorously stirred, each portion being allowed to dissolve before addition of the next. The rate of solution depended on the state of division of the lime and the temperature of the solution—the finer the powder and the lower the temperature the more rapid the solution. After 4 days no more lime would dissolve. A slight excess of lime was then added, the mixture stirred for 6 hours and allowed to settle overnight, and the solution siphoned off through a purified cotton-wool filter. In absence of carbon dioxide the solution may be kept for months without change.

By titration with 0·049*N*-hydrochloric acid and phenolphthalein, the amounts of calcium oxide in two solutions thus prepared were found to be 11·7 and 12·3 g. per litre. Calculated from the sucrose content, $[\alpha]_D^{18.5^\circ} = +53.3^\circ$ and $+53.0^\circ$. Muntz (*Z. Ver. deut. Zuckerind.*, **26**, 737) found for a 10% sucrose solution (1 mol. CaO : 1 mol. $C_{12}H_{22}O_{11}$) $[\alpha]_D = +56.9^\circ$ and (2 mols. CaO : 1 mol. $C_{12}H_{22}O_{11}$) $[\alpha]_D = +51.8^\circ$. By extrapolation, our figure for the latter value is $+51.12^\circ$.

Monolime-monosucrose.—Following Peligot's method (*loc. cit.*), 0·9 mol. of calcium oxide was added to 1·0 mol. of sucrose in 5% aqueous solution. On the addition of 500 c.c. of 60% alcohol to 200 c.c. of this solution, an amorphous white precipitate was produced, which, after drying between filter-papers, amounted to 60% of the theoretical yield of $C_{12}H_{22}O_{11},CaO,2H_2O$ (Found: CaO, 12·9; H_2O, 7·9. Calc. for $C_{12}H_{22}O_{11},CaO,2H_2O$: CaO, 12·9; H_2O, 8·3%). These figures, however, appear to be fortuitous, since small changes in the proportion of calcium oxide and sucrose are accompanied by changes in the composition of the precipitate. Moreover, if the precipitate be triturated repeatedly under 60% alcohol, the percentage of calcium oxide gradually rises and after nine triturations becomes constant (Found: CaO, 24·5. Calc. for $C_{12}H_{22}O_{11},2CaO$: CaO, 24·7%).

By the evaporation of 150 c.c. of the above aqueous solution at 0° in a vacuum over phosphoric oxide during a period of 3 months, a syrupy mass containing microscopic crystals was obtained. After it had been washed successively with conductivity water at 0°, with 50% alcohol, and again with water, and then dried between filter papers, there remained about 4 g. of slightly sticky solid (Found CaO, 11·6, 11·9; H_2O, 20·05. Calc. for $C_{12}H_{22}O_{11},CaO,5H_2O$ CaO, 11·5; H_2O, 18·45. Calc. for $C_{12}H_{22}O_{11},CaO,6H_2O$: CaO 11·2; H_2O, 21·3%). On being ground with 60% alcohol, th

product behaved in a similar manner to the dihydrate, dilime-monosucrose being formed. Monolime-monosucrose is an unstable substance at room temperature.

Dilime-monosucrose.—The white precipitate formed by mixing 500 c.c. of 60% alcohol with 250 c.c. of the lime-saturated sugar solution (p. 956) at 0° was rapidly collected, washed and triturated with 60% alcohol, and dried between filter-papers. A thin layer of the product contained in a copper boat was heated at 100° under 1 mm. pressure in a slow current of air purified by passage through soda-lime and phosphoric oxide. This operation proved very lengthy, constant weight being attained only after 35 days in one experiment, and 32 days in another. The time may be shortened very much if, after the grinding with 60% alcohol, the precipitate is ground with small quantities of pyridine and finally with absolute alcohol several times before being heated under reduced pressure. During these operations some of the product appeared to become crystalline. We are indebted to Dr. R. Campbell for an examination of the substance, which he found to be isotropic, showing conchoidal fracture but no definite cleavage, and a refractive index between 1·5245 and 1·5294. The refractive indices for sucrose crystals are α 1·5397, β 1·5667, and γ 1·5716, so there can be no question of its identity with sucrose. The solubility of the crystalline part of the product was 45·23 g. per litre, and that of the amorphous precipitate was 37·7 (calc. as $C_{12}H_{22}O_{11},2CaO,6H_2O$). (Lippmann, *O.Z. Zuckerind.*, 9, 35, gave the solubility as 1 in 33 of water.) $[\alpha]_D^{17°} = +32{\cdot}1°$ in 2·5% aqueous solution (Found: H_2O, 18·7, 17·8. Calc. for $C_{12}H_{22}O_{11},2CaO,6H_2O$: H_2O, 19·2%. Found: CaO, 24·2; C, 31·65; H, 4·8. Calc. for $C_{12}H_{22}O_{11},2CaO$: CaO, 24·6; C, 31·7; H, 4·85%).

Trilime-monosucrose.—This substance began to separate as a white precipitate from the lime-saturated sucrose solution (p. 956) when this was heated to 58°; on further heating to 80°, the precipitate settled and was easily collected on a hot funnel. It was thoroughly washed with hot conductivity water and then dried between filter-papers. Dehydration and analyses were carried out as described above [Found: H_2O, (1) constant after 66 days, 17·25, (2) constant after 56 days, 16·45; CaO, 33·0; C, 28·2; H, 4·45. Calc. for $C_{12}H_{22}O_{11},3CaO,6H_2O$: H_2O, 17·5%. Calc. for $C_{12}H_{22}O_{11},3CaO$: CaO, 33·0; C, 28·2; H, 4·3%]. An attempt to obtain this substance in crystalline form was made by sealing up some lime-sucrose solution in a tube, which was then immersed in a large volume of water. During a period of 8 days the temperature of the water was gradually raised from 17° to 58° and then more slowly to 72°. The precipitate was examined in the tube with the aid of a

lens at intervals during the heating, and thereafter on a slide under a microscope, but no crystalline structure was observed.

Although trilime-monosucrose probably does not dissolve as such in water, the amount of lime in a saturated solution obtained by mixing anhydrous trilime-monosucrose with conductivity water at 15° was found to correspond to 15·33 g. of anhydrous trilime-mono sucrose per litre (Lippmann, *loc. cit.*, records 10 g. per litre). $[\alpha]_D^{15°} = +36·52°$ for this solution.

After it had been proved by qualitative experiments that both lime and sucrose in an aqueous solution of trilime-sucrose diffuse through collodion membrane, two experiments, in which 50 c.c. of trilime-sucrose solution were placed in a collodion membrane suspended in 100 c.c. of conductivity water, were carried out with the following results :

	Sucrose.	Lime.	Sucrose : lime.
(1) Initial conc. per 100 c.c.	0·6706	0·3294	2·03
Conc. after 12 hours	0·4201	0·1187	3·56
(2) Initial conc. per 100 c.c.	0·6706	0·3294	2·03
Conc. after 24 hours	0·5129	0·1534	3·34

In the hope that methyl sulphate might react with trilime-monosucrose and produce a trimethylsucrose, methylation experiments were performed, but the products were always mixtures of more highly methylated sucroses. Some oxidation experiments, with calcium permanganate as oxidising agent, led to no definite conclusions.

Higher Lime-sucrose Compounds.—Amorphous, white precipitates were obtained on heating sucrose solutions in which less lime than that required for saturation had been dissolved. For instance, a 5% sucrose solution containing 8 g. of lime per litre gave a precipitate on heating, which, after being triturated three times with 60% alcohol and dried, appeared to have the composition $C_{12}H_{22}O_{11},4CaO,H_2O$ (Found : CaO, 38·4. Calc. : 38·4%). In another experiment starting with the same solution, the precipitate was shaken with 90% alcohol for 2 hours and then dried (Found : CaO, 38·35%). In a third experiment with 5% sucrose solution containing 5 g. of lime per litre, the precipitate after three triturations with 60% alcohol and drying gave CaO, 58·5 (Calc. for $C_{12}H_{22}O_{11},9CaO,H_2O$: CaO, 58·3%). After repeated triturations of this same precipitate with alcohol, the lime content rose (Found : CaO, 79·6%). Similar results were obtained with the other precipitates, the lime content rising to 80—90%.

Sucrose-potassium Chloride.—This colourless crystalline compound was prepared by mixing solutions of sucrose (1 mol.) and of potassium chloride (1 mol.) in the minimum quantities of boiling water. The mixture, on cooling over sulphuric acid in a vacuum

desiccator, deposited crystals (Found: KCl, 16·5; Cl, 7·8. Calc. for $C_{12}H_{22}O_{11},KCl,2H_2O$: KCl, 16·5; Cl, 7·8%). Violette (*Compt. rend.*, 1873, **76**, 485) gives the formula $C_{12}H_{22}KClO_{11}$, but without any analytical data, and describes the crystals as being isomorphous with those of sucrose itself—a very curious coincidence!

Monostrontia-monosucrose.—200 C.c. of 20% sucrose solution, in which strontia (1 mol.) had been dissolved at 75°, were shaken vigorously while being cooled: the hexahydrate was obtained in bunches of short, needle-like crystals. If the solution was allowed to cool undisturbed, or if seeded with a crystal of strontium hydroxide, crystals of the latter separated. After drying between filter-papers, the product appeared to be the hexahydrate. The solubility was 43·95 g. per litre at 16°, calculated as $C_{12}H_{22}O_{11},SrO$, and the solution showed $[\alpha]_D^{16°} = + 42·09°$. Scheibler (*N.Z. Rübenzuckerind.*, **10**, 229) gives for the solubility the interpolated figure 43·9 (Found: H_2O, 17·8; SrO, 18·7; C, 32·3; H, 4·9. Calc. for $C_{12}H_{22}O_{11},SrO,6H_2O$: H_2O, 19·5; SrO, 18·7%. Calc. for $C_{12}H_{22}O_{11},SrO$: C, 32·3; H, 4·9%). In a diffusion experiment (compare p. 958) 20 c.c. of solution were placed in a collodion membrane suspended in 50 c.c. of conductivity water. The initial concentration per 100 c.c. was sucrose 3·28, strontia 0·993 (ratio, 3·3) and the concentration after 24 hours was sucrose 1·50, strontia 0·163 (ratio, 9·21).

Distrontia-monosucrose.—To a boiling, 15% sucrose solution, strontia (slightly more than 3 mols.) was added and ebullition continued for 2 minutes. (With prolonged boiling, the precipitate becomes more difficult to filter.) The clear solution was decanted from the precipitate, which was washed with hot 10% strontia solution until colourless and then with boiling water, and dried between filter-papers or in a vacuum desiccator (Found: SrO, 37·6; C, 26·75; H, 3·4. Calc. for $C_{12}H_{22}O_{11},2SrO$: SrO, 37·7; C, 26·2; H, 4·0%). The solubility was found to be 11·89 g. per litre at 100° (Sidersky, *Bull. Asoc.*, **3**, 240, gives 1 in 84 at the boiling point). $[\alpha]_D^{15°} = + 37·79°$ for this solution cooled to 15°. The dry preparation remains unchanged for a long period, but in presence of cold water the white sandy crystals break up, monostrontia-monosucrose and strontium hydroxide being produced.

In experiments designed to obtain higher strontia-sucroses, mixtures of either or both of the above compounds with strontium hydroxide were obtained.

Monobaryta-monosucrose.—This compound appears to be the only combination of baryta with sucrose and was obtained in the anhydrous state by several methods. (*a*) To a 5% sucrose solution saturated at room temperature with baryta, an equal volume of

60% alcohol was added. The white granular precipitate which separated was filtered off, washed with 60% alcohol, and dried between filter-papers. (*b*) On boiling the 5% sucrose–baryta solution (*a*), the same precipitate was formed. (*c*) By shaking a saturated solution of sucrose with excess of powdered baryta for 10 minutes and seeding the filtered liquid with a crystal from a previous preparation, a copious crop of monobaryta-monosucrose crystals was produced (Found: BaO, 31·1; C, 29·05; H, 4·4. Calc. for $C_{12}H_{22}O_{11}$,BaO: BaO, 30·95; C, 29·1; H, 4·4%). Solubility, 22·10 g. per litre of solution at 20° (Peligot, *Ann. Chim.*, 1858, **54**, 379, gave 21·0 at 15°). $[\alpha]_D^{20°} = +43·89°$ for this solution. Dr. R. Campbell kindly examined the small crystals and reported them to be prismatic in habit, showing straight extinction and very weak double refraction.

In a diffusion experiment (compare p. 958) in which 20 c.c. of solution were placed in a collodion membrane suspended in 50 c.c. of water, the initial concentration per 100 c.c. was sucrose 1·38, baryta 0·62 (ratio, 2·22) and the concentration after 24 hours was sucrose 0·67, baryta 0·325 (ratio, 2·08).

Monolime-monoglucose.—The rapid decomposition of glucose in presence of alkali and water renders the preparation of this compound difficult. Within 1 hour lime (1 mol.) was added to 500 c.c. of 5% glucose solution at 0°, the solution filtered, and the filtrate mixed with an equal volume of 60% alcohol. The white precipitate formed was repeatedly triturated with small volumes of 60% alcohol, dried between filter-papers, and ground with absolute alcohol several times and finally with ether. It is essential to carry out these processes rapidly. Even after drying over phosphoric oxide the compound appears to be the monohydrate (Found: CaO, 21·6. Calc. for $C_6H_{12}O_6$,CaO,H_2O: CaO, 22·05%). This white amorphous powder remains unchanged for months; but if wetted, it decomposes over-night.

Attempts to isolate other hydrates gave inconclusive results. For instance, after the precipitate first produced when the lime–glucose solution and 60% alcohol were mixed had been dried between filter-papers, the lime content was 12·0% (Calc. for $C_6H_{12}O_6$,CaO,13H_2O: CaO, 11·9%). As mentioned above, by treatment with alcohol and ether, this precipitate eventually gives a monohydrate when dried over phosphoric oxide. If instead of phosphoric oxide, calcium chloride is used, the dihydrate appears to be the product (Found: CaO, 20·6. Calc. for $C_6H_{12}O_6$,CaO,2H_2O: CaO, 20·6%). A 5% glucose solution was shaken with excess of lime for 15 minutes and rapidly filtered and its rotation and lime content were measured. $[\alpha]_D^{18°} = +40·5°$ and CaO, 0·435 g. per

100 c.c. of solution. After removal of the lime by precipitation as oxalate the solution showed $[\alpha]_D^{15^\circ} = 52\cdot3^\circ$, whereas the value for the original 5% glucose solution was $[\alpha]_D^{15^\circ} = 52\cdot5^\circ$. Owing to the rapid decomposition of the solution, no consistent results were obtained in solubility measurements.

Attempts to prepare Compounds of Lime, Strontia, and Baryta with α- and β-Methylglucosides.—α-Methylglucoside, m. p. 165°, $[\alpha]_D^{15^\circ} + 157^\circ$, prepared by Fischer's method as modified by Bourquelot (*Ann. Chim.*, 1915, 3, 298), and β-methylglucoside, m. p. 108°, $[\alpha]_D^{15^\circ} - 33^\circ$, obtained by Maquenne's method (*Bull. Soc. chim.*, 1905, **33**, 469), were used in these experiments.

A mixture of 1·94 g. of α-methylglucoside in 100 c.c. of aqueous solution and 0·56 g. of lime was shaken vigorously for 6 hours. Alcohol (4 c.c.) was added to 5 c.c. of the filtered liquid and the gelatinous precipitate was rapidly collected and dried over calcium chloride in a vacuum desiccator. A small quantity of lime was the ultimate product. From the alcoholic filtrate, α-methylglucoside was recovered unchanged.

The experiment was repeated at 0° and the period of shaking extended over a month. It was also performed with a ten times more concentrated solution. Acetone was also used in place of alcohol. In each case, the lime and the glucoside were recovered unchanged.

Solutions of the glucoside, saturated at room temperature with lime, strontia, and baryta, respectively, were heated to boiling point. No visible change was apparent except in the lime solution, which became turbid owing to the decreased solubility of lime in hot water.

Measurements of the rotations of the solutions before and after the addition of the alkaline earths showed no change.

Similar experiments with β-methylglucoside produced negative results.

Monolime-monofructose.—The hexahydrate was prepared according to Winter's method (*loc. cit.*) (Found: CaO, 16·2. Calc. for $C_6H_{12}O_6,CaO,6H_2O$: CaO, 16·3%). The colourless needle-shaped crystals were examined by Dr. R. Campbell and found to show oblique extinction and feeble double refraction and to be either mono- or tri-clinic. In a vacuum desiccator at 9° over concentrated sulphuric acid, the hexahydrate loses four molecules of water (Found: H_2O, 20·9; CaO, 20·6. $C_6H_{12}O_6,CaO,6H_2O - 4H_2O$ requires H_2O, 20·9. $C_6H_{12}O_6,CaO,2H_2O$ requires CaO, 20·6%). This hydrate is fairly stable and it was not found possible to remove all the water. Solubility at 15°, 0·847 g. (calculated as $C_6H_{12}O_6,CaO,H_2O$) per 100 c.c. $[\alpha]_D^{15^\circ} = -39\cdot05^\circ$.

Efforts to prepare higher lime-fructoses showed the formation of precipitates of mixtures of lime and monolime-monofructose.

β-Methylfructoside and the Hydroxides of the Alkaline Earths.—β-Methylfructoside was prepared according to the method of Hudson and Brauns (*J. Amer. Chem. Soc.*, 1916, **38**, 1216). The first intermediate product—tetra-acetyl fructose—showed m. p. 130° and $[\alpha]_D^{15°}$ − 92·5°, whereas Hudson and Brauns's data are m. p. 120—130° and $[\alpha]_D^{15°}$ − 92·30°. The next product—tetra-acetyl methylfructoside—gave m. p. 75° and $[\alpha]_D^{15°}$ − 124°, the corresponding figures of Hudson and Brauns being 75—76° and −124·6°. The β-methylfructoside was obtained in faintly yellow crystals, readily soluble in water and in alcohol, and with difficulty in benzene; m. p. 119°, $[\alpha]_D^{15°}$ − 171°. Hudson and Brauns found m. p. 119—120° and $[\alpha]_D^{15°}$ − 172·1°.

Similar experiments to those done with α- and β-methylglucosides were performed (compare p. 961), but no evidence of the formation of compounds with the alkaline earths was forthcoming. The rotation of solutions of the fructoside was unaffected by the addition of the alkaline earths.

Monolime-monomaltose.—The preparation of this substance was carried out in the same manner as that of lime-glucose. The amorphous, white powder obtained probably is hydrated and even after drying over phosphoric oxide in a vacuum at 0°, still shows the presence of water (Found: CaO, 13·8. Calc. for $C_{12}H_{22}O_{11}$,CaO: CaO, 14·1%. Calc. for $C_{12}H_{22}O_{11}$,CaO,H_2O: CaO, 13·5%). The solubility of the monohydrate is 18·9 g. per litre, and the rotation of the saturated solution $[\alpha]_D^{15°}$ + 120·4°. The rotation calculated for the maltose in the solution is $[\alpha]_D^{15°}$ + 146·4°, whereas a pure maltose solution shows $[\alpha]_D^{15°}$ + 137·9°.

β-Methylmaltoside and the Alkaline Earths.—β-Methylmaltoside was prepared according to the method of Koenigs and Knorr (*Ber.*, 1901, **34**, 4343), ten times the quantities employed by these investigators being used. A mixture of 500 c.c. of red fuming nitric acid and 750 c.c. of chloroform was added to a solution of 50 g. of maltose octa-acetate (m. p. 157°), and the whole gently stirred for 2½ hours, the temperature throughout being kept below −5°. The product was then poured on ice, and the chloroform solution separated from the water solution and washed successively with water, sodium bicarbonate solution and water—all at 0°. After the solution had been dried by sodium sulphate, the chloroform was distilled off and the residue dissolved in ether. From the ethereal solution there separated 27 g. of colourless crystals of acetonitromaltose, m. p. 94° (Koenigs and Knorr, 93—94°).

On further concentration of the mother-liquor, a yellow oil, which

became crystalline on standing for two days at 0°, was obtained. This product, after recrystallisation from chloroform–ether, showed m. p. 178° and $[\alpha]_D^{15°}$ initially + 79·3° in chloroform and, after addition of a trace of ammonia, finally + 110·4°. The crystals were free from nitrogen [Found: $CH_3 \cdot CO$, 47·15. Calc. for $C_{12}H_{15}O_{11}(CO \cdot CH_3)_7$: $CH_3 \cdot CO$, 47·3%]. Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1871) gives the melting point of maltose hepta-acetate as 181° and $[\alpha]_D^{20°}$ initial + 67·8°, final + 111°. The hepta-acetate appears to have been produced by the hydrolysis of some of the acetonitromaltose.

From 26 g. of acetonitromaltose, 15 g. of hepta-acetylmethyl-maltoside were obtained in colourless crystals, m. p. 128°, $[\alpha]_D^{15°}$ + 53·6° in 2·5% chloroform solution (Koenigs and Knorr, m. p. 129°; Hudson, $[\alpha]_D$ + 53·8°).

The deacetylation of 15 g. of hepta-acetylmethylmaltoside by Helferich and Becher's method (*Annalen*, 1924, **440**, 17) gave 3·8 g. of crystals, m. p. 105°, $[\alpha]_D^{20°}$ + 75·7° in 1·355% aqueous solution (Helferich and Becher give m. p. 105° and $[\alpha]_D^{19°}$ + 76°).

On saturating the methylmaltoside solution with baryta, strontia, and lime respectively, a very slight fall in the rotation (0·02°) was observed in the first two cases and no change in the last. The recovered methylmaltoside was recrystallised from alcohol–ethyl acetate: the rotation rose to $[\alpha]_D^{15°}$ + 82·5°, the calculated value being + 85°.

Monolime-monolactose.—The preparation was carried out in the same manner as that of the maltose compound. No definite hydrate was obtained, and decomposition took place when moisture was present. The dry substance may, however, be kept for weeks without appreciable change (Found: CaO, 13·9. Calc. for $C_{12}H_{22}O_{11}$,CaO: CaO, 14·1%). The solubility of the white amorphous powder was 18·6 g. per litre of solution, and this solution gave $[\alpha]_D^{15°}$ + 46·06°. These numbers are, however, only approximately correct, decomposition setting in immediately the substance has dissolved.

Efforts to obtain higher lime-lactoses were fruitless.

β-Methyl-lactoside and the Hydroxides of the Alkaline Earths.—Anhydrous lactose was converted into acetobromolactose by Dale's method (*J. Amer. Chem. Soc.*, 1916, **38**, 2187). Yield, 60% of the theoretical. M. p. 140°. $[\alpha]_D^{20°}$ in chloroform = + 106·5°. E. and H. Fischer (*Ber.*, 1910, **43**, 2521) give m. p. 143—144° and $[\alpha]_D^{20°}$ + 104·9°.

From the acetobromolactose, hepta-acetylmethyl-lactoside was obtained by the action of methyl alcohol and silver carbonate (Ditmar, *Monatsh.*, 1902, **23**, 865). The product was without action

crystalline condition. This is decomposed by ammonia with the separation of the free acid, $C_{21}H_{26}O_3N_2$, which melts at 285° with elimination of water and regeneration of dihydrostrychnine (B), a series of changes reminiscent of the conversion of strychnine into strychnic acid and the regeneration of the base from the latter by the action of heat.

This behaviour clearly proves that the oxidation product of dihydrostrychnidine (B) contains the group >N⁻CO⁻ and the reactions of the substance (see p. 981) show that it is the group >N(*a*)⁻CH_2⁻ and not the group >N(*b*)⁻CH_2⁻ that has been transformed (compare J., 1928, 3087, 3090). A substance containing >N(*a*)⁻CH_2⁻ and >N(*b*)⁻CO⁻ would be expected to show the reactions of the strychnidine type, whereas an isomeride containing >N(*a*)⁻CO⁻ and >N(*b*)⁻CH_2⁻ would resemble strychnine. Actually the substance $C_{21}H_{24}O_2N_2$, m. p. 196°, shows the characteristic reactions of strychnine and fails to exhibit those characteristic of strychnidine.

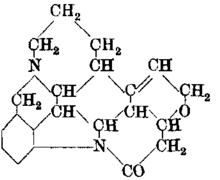
Dihydrostrychnine (B) is unchanged by reagents for the carboxyl and hydroxyl groups and it is therefore evident that its condensation with benzaldehyde must involve the change >N(*a*)·CO·CH_2⁻ ⟶ >N(*a*)·CO·Ċ:CHPh, and it is worthy of note that such a process should be so facile. Analogies are forthcoming in the well-known ready formation of the arylidene derivatives of oxindole and in the condensation of derivatives of piperidone with reactive esters such as ethyl oxalate, ethyl cinchoninate, or ethyl nicotinate (Ruzicka, *Helv. Chim. Acta*, 1921, **4**, 472, 482, 486; compare also Späth and Bretschneider, *Ber.*, 1928, **61**, 327).

The above interpretation of the nature of dihydrostrychnine (B) and the discovery of its benzylidene derivative suggested that dihydrostrychnine (A) and strychnine itself also might condense with benzaldehyde, and this was found to be indeed the case. A detailed account of these accessible strychnine derivatives, important on account of the new breach in the defences against oxidising agents, is reserved, but we have included a brief description of *benzylidene-strychnine* in this communication. The formation of this substance proves that strychnine contains the group >N(*a*)·CO·CH_2⁻, and this was not previously known with certainty.

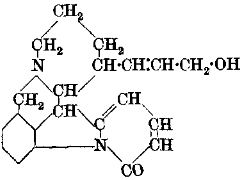
Dihydro*iso*strychnine does not, however, appear to condense with benzaldehyde to form a characteristic derivative analogous to the benzylidenedihydrostrychnines (A) and (B). This would be explicable if the strychnine–*iso*strychnine change involved the transformation

>N(*a*)⁻CO·CH_2—CH< ⟶ >N(*a*)·CO·CH═C<

This simple change is difficult to bring into line with the fact that dihydro*iso*strychnine does not absorb hydrogen in the presence of palladium (compare Part VI, *loc. cit.*, p. 2398) and in order to accommodate this observation we have considered the possibility that a further ring-fission occurs, giving a true pyridone which might well offer resistance to catalytic hydrogenation. The scheme given below on the basis of one of the formulæ * recently discussed (J., 1928, 3089) has the advantage that it explains why the strychnine–*iso*strychnine change has no parallel among strychnidine derivatives and it also serves to relate this change to the formation of brucinolone.



Strychnine.



iso*Strychnine.*

The conversion of dihydrostrychnine (A) into dihydro*iso*-strychnine can be represented in an entirely similar manner and the assumption that either a saturated or an unsaturated group can break away from the potential pyridone nucleus does not involve any theoretical difficulty. It is analogous to the migrations of saturated alkyl or unsaturated aryl groups in molecular re-arrangements. Preliminary experiments on the oxidation of dihydrostrychnidine (A) (Part VI, J., 1927, 2399) with permanganate suggest that this substance behaves similarly to the isomeride (B) only in regard to the composition of the product, since it yields *oxydihydrostrychnidine (A)*, $C_{21}H_{24}O_2N_2$, m. p. 345°, a substance which has not yet been further investigated but is clearly not identical with dihydrostrychnine (A).

When dihydrostrychnine (B), m. p. 196°, is treated with hydrogen

* The point of attachment of the ether oxygen given in the formulæ put forward in this memoir was based on a misapprehension of the facts and requires modification. The heterocyclic ring should be 6-membered and the oxygen should be joined to C 17 and not to C 18, because Leuchs and his collaborators found that the brucinolone, which is the primary product of the decomposition of brucinolic acid, contains the group >N·CO·CH:C<. In subsequent changes the ethylene linkage moves into the βγ-position and then back again into the position indicated; the change is accompanied by another transformation in some other portion of the molecule.—R. C. F., W. H. P., R. R.

is the reverse of that which occurs when dihydrostrychnidine (B) is converted, by the action of alcoholic potash on its methochloride, into methoxymethyltetrahydrostrychnidine (B). When the hydriodide of the isomeride, m. p. 220°, is heated, a change similar to that shown above takes place (compare Part IV, J., 1927, 1618; Part VI, *ibid.*, p. 2410), but the yield is extremely small and preliminary experiments on the action of boiling hydriodic acid on the base seem to show that in this case also the transformation takes place with difficulty and only to a small extent. It is difficult to understand why the two isomerides, m. p. 180° and 220°, should show such very different behaviour in these and some other parallel circumstances.

In describing the action of methyl-alcoholic potash on the methochloride or dimethochloride of dihydrostrychnidine (B) (p. 985), it is shown that the product of this decomposition consists essentially of methoxymethyltetrahydrostrychnidine (B) (m. p. 180°). The mother-liquors which had accumulated from many preparations of this substance contained some dihydrostrychnidine (B) and two new substances, namely, *methyl-ψ-strychnidine (B)* * (m. p. 225°) and *dihydrostrychnidine (C)* (m. p. 134°), isomeric with (A) (m. p. 212°) and (B) (m. p. 151°). The formation of dihydrostrychnidine (B) from its methochloride by the action of methyl-alcoholic potash is clearly due simply to the removal of methyl chloride, and this takes place only to a very small extent. A similar change occurs quantitatively when the methochloride of dihydrostrychnidine (C) is heated with methyl-alcoholic potash (see below). Methyl-ψ-strychnidine (B), $C_{22}H_{26}ON_2$ (m. p. 225°) is a sparingly soluble substance yielding a well-crystallised *dimethiodide*, $C_{22}H_{26}ON_2,2MeI$, and a solution of the dimethochloride exhibits a very characteristic behaviour on evaporation, becoming intensely purple. Dihydrostrychnidine (C), $C_{21}H_{26}ON_2$ (m. p. 134°), crystallises from ether in brilliant prisms which Dr. T. V. Barker has kindly examined and measured. On treatment with methyl iodide, it gradually yields a *dimethiodide*, $C_{21}H_{26}ON_2,2MeI$; the *dimethochloride*, obtained from this by the action of silver chloride, is completely decomposed on heating with methyl-alcoholic potash, with regeneration of dihydrostrychnidine (C).

It is evident from the results recorded above that the differences existing between dihydrostrychnidines (A) and (B) either are stereochemical or more probably originate in an isomeric change of

* In proposing this name in order to distinguish the new base, we do not imply that there is necessarily any structural relation or analogy with the compound previously termed methyl-ψ-strychnidine.

the ring system under the influence of the drastic treatment to which the base is subjected.

The change might be in the position of a bridge ring, in the shift of a link so that a fused 5-ring : 6-ring system becomes 6-ring : 5-ring, or in a buckling or ring contraction such that, for example, $-CH_2 \cdot CH_2-$ becomes $-CHMe-$ and a 6-ring becomes a 5-ring. The formation of benzylidenedihydrostrychnine (B) shows that this contraction, if it occurs, does not affect the group $>N(a)-CH_2-CH_2-$. We have no clue to the precise nature of the isomerism, but the behaviour of methoxymethyltetrahydrostrychnidine (B) towards hydriodic acid indicates that the heterocyclic system including $>N(b)-$ is more stable in dihydrostrychnidine (B) than in its isomeride (A).

Pursuing this line of argument, it would appear that the system in dihydrostrychnidine (C) is more stable still, because in this case the ring cannot be opened at all.

These conclusions are not easy to utilise in any definite manner, but they do imply that the strychnine carbon skeleton must be such that it can be modified in two ways so as to reach its most stable arrangement. Such modifications may be collateral or consecutive.

This communication also contains a short account of some new derivatives of strychnidine which are at present under examination.

The preparation of *strychnidine dimethosulphate*,

$$C_{21}H_{24}ON_2,2Me_2SO_4,$$

is described and its conversion into the corresponding *dimethiodide* and *dimethochloride*, and also the preparation of *strychnidine benzylchloride*, $C_{21}H_{24}ON_2,C_7H_7Cl$, and its conversion by the action of methyl-alcoholic potash into *methoxybenzyldihydrostrychnidine*, $C_{29}H_{34}O_2N_2$.

EXPERIMENTAL.

Preparation of Dihydrostrychnidine (B), $C_{21}H_{26}ON_2$.—Carefully purified strychnidine (25 g.) is mixed with hydriodic acid (100 c.c.; *d* 1·94) and amorphous phosphorus (8 g.) in a flask fitted with a wide ground-in condenser, and the mixture is gradually heated on a sand-bath and then boiled for 24 hours, care being taken to avoid stoppage of the condenser tube by phosphonium iodide. The almost colourless liquid, after filtering through asbestos to remove any phosphorus, is mixed with saturated sulphurous acid (100 c.c.), causing the separation of a thick brown paste. On the addition of water (500 c.c.) and thorough shaking, the brown precipitate becomes yellow. When the liquid is now boiled, much of the precipitate dissolves and the whole becomes colourless. After cooling, the clear solution is filtered from an insoluble iodide (8–10 g.; not

further examined), made strongly alkaline with caustic potash, and extracted three times with ether; the ethereal solution is well washed several times with water (A; see below), dried over potassium carbonate, and evaporated; a pale yellow gum (13 g.) then remains, which on standing becomes a partly crystalline sticky mass. The separation of pure dihydrostrychnidine (B) from the crude product, owing to its small tendency to crystallise when in this condition, is a tedious process, but may be done in either of the following ways.

(i) The well-dried concentrated solution in pure ether is left in a closed flask in the ice-chest for several days in contact with a few crystals of the substance. A pale yellow crust of prisms gradually forms and this is recrystallised several times from pure dry ether until the substance melts at 145—148°.

(ii) The crude product is digested with a large volume of petroleum (b. p. 60—80°), and the solution is filtered, concentrated, and kept in the ice-chest; the crystalline crust that gradually forms is recrystallised until the pale yellow prisms melt at 145—148°. In view of the fact that the base is almost insoluble in water it is very difficult to understand why, during the washing of the etherea solution of the crude base with water, about 25% of the substanc passes into the washings (A). When these are concentrated b distillation under reduced pressure and then by evaporation on th steam-bath, a syrup separates which sets to a resin on cooling. Thi is washed and dissolved in pure ether and the solution is dried ove potassium carbonate, concentrated, and left in the ice-chest a crust of colourless glistening prisms then gradually separates whic after recrystallisation melts at 146—148° and consists of dihydr strychnidine (B) (Found: C, 78·3; H, 8·3%. See below).

In either case (i) or (ii), the mother-liquors are evaporated and th viscid syrup is distilled; almost the whole passes over at 225-227°/0·2 mm. and treatment with petroleum then gives a furth small quantity of the crystalline base. The distillation and th treatment with petroleum are continued until there is no furth crystallisation. It is curious that the final syrup gives analytic numbers agreeing closely with those required for the formu $C_{21}H_{26}ON_2$ (Found: C, 78·2; H, 8·5%) and is converted into t dimethiodide of dihydrostrychnidine (B) (compare p. 977) when solution in methyl alcohol is boiled with a large excess of meth iodide.

Dihydrostrychnidine (B) crystallises in brilliant colourless pris which do not melt quite sharply but usually soften at 145° and molten at 151° (Found: C, 77·9, 78·3; H, 8·1, 8·2; N, 8 $C_{21}H_{26}ON_2$ requires C, 78·2; H, 8·1; N, 8·7%). It is unfortun

that the facets of the crystals are not sufficiently well developed to allow of accurate crystallographical measurement. The base is very soluble in alcohol or benzene, less soluble in acetone or ether, and almost insoluble in water. It crystallises well from acetone but appears to suffer some change on long boiling with this solvent; from ether it separates usually in short, hard, glistening prisms but sometimes in groups of striated needles. It is a strong base and a solution in dilute sulphuric acid gives (i) with dichromate at first a faint red colour, deepening on standing or warming to reddish-brown, and (ii) with nitrite an orange colour rapidly becoming brown. The base, dissolved in very dilute hydrochloric acid, gives with ferric chloride no coloration at first, but gradually a pink colour develops which becomes crimson on warming. A solution in dilute acetic acid combines with diazobenzenesulphonic acid to give a yellow solution, becoming intensely crimson on addition of hydrochloric acid.

In order to determine whether dihydrostrychnidine (B) contains a keto-group, its behaviour (i) with hydroxylamine, (ii) towards sodium and alcohol, and (iii) towards electrolytic reduction was investigated.

(i) The base (2 g.), dissolved in alcohol, was mixed with hydroxylamine hydrochloride (5 g.) and sodium acetate (5 g.) and boiled under reflux for 2 hours. The reaction mixture was kept over the week-end, caustic potash then added, and the whole extracted with ether. The washed and dried ethereal solution deposited, on concentration, the unchanged base in prisms (1·5 g., m. p. 145—147°).

(ii) Sodium (20 g.) was rapidly added to a solution of the base (10 g.) in boiling alcohol (350 c.c.). When the whole of the sodium had dissolved, water was added, the base extracted with ether, the ethereal solution well washed, dried over potassium carbonate, and evaporated, and the colourless syrup distilled. The whole passed over at 225—230°/0·4 mm. When it was dissolved in a little ether and left in the ice-chest in contact with a crystal of the original base, a crust of crystals of the unchanged substance, m. p. 145—147°, gradually separated (Found: C, 78·4; H, 8·3%).

(iii) The base, dissolved in 10% sulphuric acid, was placed in the electrolytic apparatus described in Part IV (J., 1927, 1600), and a current of 5 amps. passed for 12 hours. The colourless solution was mixed with caustic soda and extracted with ether, the ethereal solution dried over potassium carbonate and concentrated, and the base distilled. Almost the whole passed over at 225—230°/0·4 mm. as a colourless syrup; a concentrated solution of this in ether, left in the ice-chest, gradually deposited a crust of crystals of the unchanged base, m. p. 145—147°.

In order to determine whether dihydrostrychnidine (B) is capable of yielding an acetyl derivative, the base (2 g.) was digested under reflux on the steam-bath with anhydrous sodium acetate (2 g.) and acetic anhydride (6 c.c.) for 4 hours. The product was mixed with ice and left in the ice-chest over-night, but nothing separated even after addition of an excess of sodium bicarbonate. The whole was made strongly alkaline with potassium hydroxide and extracted with ether: from the dried and concentrated extract the unchanged base separated.

Attempts to condense dihydrostrychnidine (B) with aldehydes were made under the following conditions. The base (1 g.), dissolved in alcohol, was mixed with benzaldehyde (2 c.c.) and a few drops of concentrated sodium ethoxide solution and left over-night. The pasty product was heated in the water-bath for ½ hour, mixed with water, and extracted with ether, and the ethereal solution was well washed, dried over potassium carbonate, and concentrated; the unchanged base then separated in colourless prisms, m. p. 145—147°. The effect of the treatment with benzaldehyde had been merely to remove a trace of colouring matter. Similar results were obtained in experiments in which the benzaldehyde was replaced by piperonal and by salicylaldehyde.

Dihydrostrychnidine (B) *hydrochloride*, $C_{21}H_{26}ON_2,HCl,3H_2O$, separates from concentrated aqueous solution in needles and is very soluble in water. The air-dried substance lost 10·2% at 100° and then gave C, 67·3; H, 8·0; N, 7·6; Cl, 9·4 ($C_{21}H_{26}ON_2,HCl,3H_2O$, losing $2H_2O$, requires loss, 9·7%. $C_{21}H_{26}ON_2,HCl,H_2O$ requires C, 67·1; H, 8·0; N, 7·7; Cl, 9·5%). Dried at 100°, the hydrochloride melts at 123° with vigorous decomposition. Addition of ammonia to a dilute solution of the hydrochloride precipitates the base as a caseous mass which melts under water and only slowly crystallises. A concentrated ethereal solution gradually deposits the base in prisms, m. p. 144—147°.

The dihydriodide and monohydriodide. A solution of dihydrostrychnidine (B) in dilute sulphuric acid containing a little sulphurous acid was heated to boiling, and sodium iodide then added in excess: the clear solution obtained, on cooling and rubbing, deposited minute colourless warts, which, after being washed and left on porous porcelain, became sticky on the steam-bath (Found, after drying over sulphuric acid in a vacuum: C, 42·9; H, 5·0. $C_{21}H_{26}ON_2,2HI$ requires C, 43·6; H, 4·8%). This *dihydriodide* is readily soluble in hot water and sparingly soluble in cold methyl alcohol. After it has been boiled with the latter solvent for some minutes, a mass of soft needles of the *monohydriodide* separates, the boiling with methyl alcohol having removed hydrogen iodide (Found in substance

dried at 105°: C, 55·8; H, 6·6. $C_{21}H_{26}ON_2,HI$ requires C, 56·0; H, 6·0%). This hydriodide melts at about 235—240° (efferv.) and is readily soluble in, but does not appear to combine with, chloroform. When it is boiled with water (in which it is sparingly soluble) and silver chloride and the filtered solution is concentrated, the hydrochloride described above separates.

The methosulphate (*a*). When a solution of dihydrostrychnidine (B) (8 g.) in carefully dried benzene (50 c.c.) was mixed at 10° with freshly distilled methyl sulphate (4 c.c.), it clouded immediately and became warm and a jelly separated on the sides of the flask. The benzene layer was at once poured off and the jelly washed with benzene; it then rapidly crystallised. After contact with porous porcelain and drying over sulphuric acid in a vacuum, the colourless mass contained S, 7·6 ($C_{21}H_{26}ON_2,Me_2SO_4$ requires S, 7·2%). This *methosulphate* is very soluble in warm water and on addition of sodium iodide the cloudy liquid deposits a jelly which soon becomes crystalline when warmed on the steam-bath. This *methiodide* (*a*) separates from water, in which it is rather sparingly soluble, in brilliant groups of needles which gradually change to heavy, detached, striated prisms; the mother-liquor, on remaining exposed to the air, deposits the same substance in large crystals. It melts at 340—345° (decomp.),* is almost insoluble in cold acetone, but is moderately readily solnble in hot methyl alcohol, separating in prismatic needles (Fonnd: C, 57·3; H, 6·1; N, 6·1. $C_{21}H_{26}ON_2,MeI$ requires C, 56·9; H, 6·2; N, 6·0%). This methiodide is identical with the substance obtained by the action of methyl-alcoholic potash on dihydrostrychnidine (B) dimethiodide (A) (p. 979) and most of the material was made by that process. It is also identical with the substance obtained by the action of heat on the hydriodide of methoxymethyltetrahydrostrychnidine (B) (p. 988). Its most characteristic property is its behaviour with chloroform, in which the finely powdered substance dissolves completely in tbe cold; on standing, or much more rapidly on warming, crystallisation sets in with the separation of the sparingly soluble *additive* derivative. This was collected, washed with chloroform, and left on porous porcelain exposed to the air for a few minutes (Found: loss on heating at 100°, 20·2; C, 47·9; H, 5·6. $C_{22}H_{29}ON_2I,CHCl_3$ requires $CHCl_3$, 20·4; C, 47·3; H, 5·2%). This substance gradually loses chloroform on exposure to air and much more rapidly over sulphuric acid in a vacuum; in the latter case after 12 hours the substance contained only 15·7% of chloroform.

* The melting points of the methiodides described in this series of papers vary very much with the rapidity of heating and the determinations were always made rapidly in an electrically heated m. p. apparatus (Mason).

The *methochloride* (a) was obtained by grinding the methiodide (a) to a paste with warm water and digesting the mass with a large excess of silver chloride and water on the steam-bath for 2 hours. The solution was evaporated to a small bulk and left over sulphuric acid in a vacuum; a hard satiny mass of the methochloride (a) remained, m. p. 335—340° (vig. efferv.) (Found in material dried at 120°: C, 70·2; H, 8·0. $C_{21}H_{26}ON_2$,MeCl requires C, 70·8; H, 7·8%). *The action of heat.* The dry methochloride, in quantities of 0·5 g., was heated very cautiously in test-tubes until effervescence was complete and a yellowish-brown syrup remained, which set to a resin but did not crystallise. About 5 g. of this resin were distilled under 1 mm., the distillate was dissolved in pure dry ether, and the solution concentrated in a test-tube and left in the ice-chest for several days. The pale yellow prisms which gradually separated had m. p. 145—147° and consisted of dihydrostrychnidine (B), as the analysis and a mixed m. p. showed (Found: C, 78·0; H, 8·1; N, 8·6. Calc. for $C_{21}H_{26}ON_2$: C, 78·2; H, 8·1; N, 8·7%).

Dihydrostrychnidine (*B*) *dimethosulphate* (*A*) was obtained by adding methyl sulphate (5 c.c.) to a solution of the base (2 g.) in warm dry benzene (30 c.c.), shaking the mixture well and keeping it at about 30° for 24 hours. The benzene solution was decanted from the crystalline cake, which was washed with benzene, left in contact with porous porcelain, and dried over sulphuric acid in a vacuum (Found: S, 10·9. $C_{21}H_{26}ON_2,2Me_2SO_4$ requires S, 11·1%). This dimethosulphate is readily soluble in warm water. A rather dilute solution gave, with excess of sodium iodide, no precipitate (but an immediate voluminous crystalline precipitate on the addition of a large quantity of 50% caustic potash). However, the clear solution slowly deposited stars of brilliant prisms, which gradually became yellow unless a little sulphurous acid had been added (Found in material dried at 100°: C, 45·3; H, 5·4; Me as >NMe, 4·8. $C_{21}H_{26}ON_2$,2MeI requires C, 45·6; H, 5·3; 2Me as 2>NMe, 4·9%). This dimethiodide had m. p. 238—242° (decomp.) and proved to be identical with the substance produced by the direct union of the base and methyl iodide under the conditions explained on p. 977. It is very sparingly soluble in methyl alcohol or benzene but dissolves readily in cold and very readily in hot water. It is very stable and may be warmed on the steam-bath with 20% caustic potash solution for some minutes with very little decomposition. The crystals give no coloration with diazobenzenesulphonic acid and acetic acid and there is no change on the addition of hydrochloric acid. It dissolves with difficulty in chloroform and, on warming, a very sparingly soluble substance separates which has not been analysed but appears to be an additive compound (compare p. 975)

The *dimethochloride* (*A*) was obtained by adding silver chloride to a hot aqueous solution of the dimethiodide (A) and evaporating the filtrate; a syrup remained which became a transparent resin when kept over sulphuric acid in a vacuum. An aqueous solution gives no coloration with a drop of dilute hydrochloric acid and ferric chloride. An aqueous solution does not cloud when boiled with a large excess of caustic potash, and even heating with methyl-alcoholic potash (25%) on the steam-bath only very gradually brings about decomposition. When, however, the temperature is raised to 120°, a rapid change takes place with formation of methoxymethyltetrahydrostrychnidine (B), m. p. 178—180° (p. 985).

The *dimethobromide* (*A*) does not crystallise when sodium bromide is added to a moderately concentrated solution of the dimetho-chloride, but 50% caustic potash solution gives a cloudy liquid from which a mass of needles soon separates. This dimethobromide is remarkably readily soluble in cold water, but separates from methyl alcohol as a voluminous mass of needles which, dried at 100°, decompose with effervescence at about 345° (Found: C, 53·4; H, 6·5. $C_{21}H_{26}ON_2$,2MeBr requires C, 52·9; H, 6·3%).

The Action of Methyl Iodide on Dihydrostrychnidine (*B*).—It is explained in the introduction that this direct action leads to the formation mainly of the dimethiodide (A), the isomeride (B) being produced in relatively very small quantity. When the base (B) (5 g.), dissolved in a little methyl alcohol, was mixed with methyl iodide (8 c.c.) in the cold, the solution became warm and crystallisation began at once owing to the separation of the monomethiodide (*a*), m. p. 340—345° (decomp.) (Found: C, 56·8; H, 6·2%. Compare p. 975). When the mixture was heated under reflux on the steam-bath a second reaction occurred, and boiling continued for a considerable time after removal from the bath. Finally the whole was heated for 2 hours, the methyl iodide and some of the methyl alcohol were distilled off, and the product was left for 24 hours in the ice-chest; the crystalline mass was then collected and washed with methyl alcohol. Analysis and the subsequent examination showed that this crude product consists mainly of the dimethiodides (A) and (B), but contains varying quantities of the monomethiodide (a). The product (60 g.) from several experiments was boiled with methyl alcohol, in which it is sparingly soluble, until completely dissolved and the solution was cooled rapidly in running water; a sandy precipitate (40 g.) of the almost pure dimethiodide separated, there was then a distinct pause in the crystallisation, and, after filtration and vigorous shaking, glistening needles (10 g.), which had m. p. 345° (efferv.) and consisted of the almost pure monomethiodide (a),

were deposited. These crystals became opaque at 100° (Found: C, 57·2; H, 6·6. Calc. for $C_{21}H_{28}ON_2$,MeI: C, 56·9; H, 6·2%). The mother-liquor contained more of the above substances as well as all the dimethiodide (B): the separation of these constituents is described on p. 979.

The difficulty of preparing the large amounts of the dimethiodide (A) required for this research was bound up with the difficulty, already commented on (p. 972), of obtaining the requisite quantities of the crystalline dihydrostrychnidine (B). This was, however, got over when it was found that, owing to the facility with which it crystallises, it is possible to obtain the pure dimethiodide in quantity from specimens of the crude base which no longer crystallise. The mother-liquors from the crystalline base were evaporated and the residue was distilled three times; almost the whole then passed over at 220—230° under a pressure of 0·5 mm. The pale yellow syrupy distillate, which set to a resin on cooling and yielded, when dissolved in ether or extracted with petroleum, only a comparatively small quantity of crystalline dihydrostrychnidine (B), nevertheless gave analytical numbers agreeing almost exactly with those required for the formula $C_{21}H_{26}ON_2$ of this base (Found: C, 78·1; H, 8·2. Calc.: C, 78·2; H, 8·1%). As, in spite of careful search, no evidence of the presence of an isomeride could be obtained, it is probable that some slight impurity was present which prevented the separation of the crystalline base: it is known that very small quantities of impurity have this effect. The resin (50 g.), dissolved in as little boiling methyl alcohol as possible, was gradually mixed with methyl iodide (70 c.c.); a good deal of heat was then generated and crystallisation began at once. As soon as the reaction had subsided, the whole was heated under reflux for 4 hours on the steam-bath, the excess of methyl iodide distilled off, a little boiling methyl alcohol added, and the whole left over-night in the ice-chest; the mass of crystals was then collected and washed with methyl alcohol until colourless. After twice crystallising from methyl alcohol, the product (75 g. instead of 110 g.) was the pure dimethiodide (A), m. p. 340—345° (decomp.). Very little more could be got by concentrating the dark brown mother-liquors, the working up of which into methoxymethyltetrahydrostrychnidine (B) is described on p. 986.

Preparation of Dihydrostrychnidine (B) Methiodides (a) and (b).—Since it was not possible to obtain the large quantities of these substances required for this research from the corresponding methosulphates (compare p. 975), experiments were made in the hope of obtaining them by removing one molecule of methyl iodide from the dimethiodides (A) and (B). In the first experiment, the dimethiodide (A) (5 g.) was digested with mesitylene (50 c.c.) for

hour in the manner described in the corresponding conversion of methoxymethyltetrahydrostrychnidine (A) dimethiodide (B) into the monomethiodide (b) (J., *1927*, *1621*). The substance did not dissolve, and separated from methyl alcohol in colourless needles which became opaque on the steam-bath and decomposed at 340—345°. The analysis (C, 45·8; H, 5·5%) showed that elimination of methyl iodide had not occurred.

After further experiments of a similar kind, it was discovered that the desired result could be easily obtained by treating the crude dimethiodides, obtained as described on p. 977, with methyl-alcoholic potash under the following conditions: The finely powdered mixture of dimethiodides (50 g.) is ground to a fine paste with methyl-alcoholic potash (250 c.c. of 25%), heated just to boiling on the steam-bath, removed, and, after the somewhat vigorous action has subsided, heated with frequent shaking for 3 hours. The substance does not dissolve but changes in appearance, the original pasty liquid depositing a crystalline crust. After remaining for 24 hours in the ice-chest, the solid is collected and washed with methyl alcohol; it then consists essentially of the methiodide (a) containing some unchanged dimethiodide (A). A second treatment with methyl-alcoholic potash does not entirely remove this dimethiodide, but this is easily got rid of by extraction with cold water and may be recovered from the filtrate by distilling off the water under reduced pressure and crystallising the residue from methyl alcohol. The methiodide (a), sparingly soluble in water, is then crystallised from methyl alcohol, separating in colourless needles, m. p. 345° (decomp.), and is identical with the substance already described as resulting from the decomposition of the methosulphate (a) with sodium iodide (p. 975) (Found: C, 57·0; H, 6·3. Calc. for $C_{21}H_{28}ON_2$,MeI: C, 56·9; H, 6·2%).

Dihydrostrychnidine (*B*) *dimethiodide* (*B*) was present only in small quantity in the methyl-alcoholic mother-liquors from which the dimethiodide (A) and the monomethiodide (a) had separated (see p. 977), and its isolation proved to be difficult. The mother-liquor, on concentration, deposited further quantities of the above substances and then a rather sticky mass which, after long contact with porous porcelain and repeated fractional crystallisation from methyl alcohol, ultimately yielded nodules of needles of the dimethiodide (B). This decomposes at 260—265° (efferv.), is very soluble in cold water, and is more soluble in methyl alcohol than the modification (A), from which it also differs in appearance and most other properties (Found: C, 45·7; H, 5·5. $C_{21}H_{28}ON_2$,2MeI requires C, 45·5; H, 5·3%).

Dihydrostrychnidine (*B*) *methiodide* (*b*) may be prepared by

digesting the dimethiodide (B) with methyl-alcoholic potash under conditions similar to those described above in the case of the dimethiodide (A), and some was also obtained from the mother-liquors of the methiodide (a) (compare above). It separates from methyl alcohol, in which it is far more soluble than the isomeride (a), as a soft mass of needles which do not become opaque at 100°, shrink at about 250° and gradually melt as the temperature rises (Found: C, 56·2; H, 6·5. $C_{21}H_{26}ON_2$,MeI requires C, 56·9; H, 6·2%). In contrast with the methiodide (a), the substance (b) does not appear to combine with chloroform. It dissolves with difficulty in much chloroform in the cold, much more readily on boiling, and there is no sign of the separation of a sparingly soluble additive compound.

Dihydrostrychnidine (B) methochloride (b) is, in contrast with (a) (p. 976), a well-characterised substance. It was obtained in the usual way by heating the methiodide (b) with water and silver chloride on the steam-bath and evaporating the filtrate to a small bulk; on cooling, balls of needles gradually separated. These were recrystallised from water, from which the substance separated in four-sided, pearly plates containing 2 molecules of water (Found for the air-dried substance: loss at 100°, 9·45. $C_{21}H_{26}ON_2$,MeCl,$2H_2O$ requires $2H_2O$, 8·8%. Found for the dry substance: C, 70·6; H, 8·0. $C_{21}H_{26}ON_2$,MeCl requires C, 70·8; H, 7·7%). This methochloride (b) is relatively sparingly soluble in cold water. The intensely bitter solution gives, with a drop of dilute hydrochloric acid and ferric chloride, a yellow coloration soon becoming pink; on boiling, a crimson colour develops; addition of excess of hydrochloric acid destroys the colour. A solution in dilute sulphuric acid gives, with dichromate, a yellow colour slowly changing to yellowish-crimson, and to crimson on boiling. When this dimethochloride (b) was heated with methyl-alcoholic potash at 120—130° under the conditions given on p. 985, a good yield of methoxymethyltetrahydrostrychnidine (B) (m. p. 178°) was obtained.

The *methobromide* (*b*) was obtained by adding sodium bromide to a hot concentrated aqueous solution of the methochloride and leaving the mixture in the ice-chest for several days. It separated in colourless glistening plates, which became nearly black at 330° and effervesced at 340—345° (Found in substance dried at 110°: C, 63·0; H, 7·3. $C_{21}H_{26}ON_2$,MeBr requires C, 63·3; H, 7·0%).

Dihydrostrychnidine (B) Benzylchloride.—The base (6 g.), dissolved in toluene (30 c.c.), was mixed with a large excess of benzyl chloride (15 c.c.) and heated with a free flame; a precipitate soon began to separate and there was considerable rise of temperature. After boiling for a few minutes, and cooling, the product was mixed with

ether, and the colourless crystalline precipitate was collected, washed with ether, dissolved in warm methyl alcohol, and mixed with much ether; on rubbing, the clear solution deposited a mass of thin plates which were washed with ether and dried at 100° (Found: C, 74·3; H, 7·8; Cl, 7·8. $C_{21}H_{26}ON_2,C_7H_7Cl$ requires C, 74·9: H, 7·5; Cl, 7·8%).

Dihydrostrychnidine (*B*) *benzylchloride* is very soluble in cold water or methyl alcohol but almost insoluble in ether. It melts at about 325° with effervescence and formation of a yellow gum, which is insoluble in water but very soluble in cold dilute acids and appears in part to consist of dihydrostrychnidine (B). A solution in water gives no precipitate with ammonia or dilute aqueous potassium hydroxide.

Oxidation of Dihydrostrychnidine (*B*). *Formation of Dihydrostrychnine* (*B*).—The crystalline base (5 g.), dissolved in acetone (400 c.c.) and water (3 c.c.), was gradually mixed with finely powdered potassium permanganate with frequent shaking, care being taken that the temperature did not exceed 15°. The permanganate was added in quantities of 2 g. each day and, after 13 g. had been added, the whole was heated to boiling and filtered and the manganese precipitate thoroughly extracted with boiling acetone. The extract was dried over potassium carbonate, concentrated to a small bulk, and left in the ice-chest, a crystalline crust gradually forming. This was dissolved in much boiling ether, in which the crystals were rather sparingly soluble, and the solution was concentrated and left in the ice-chest; the new substance then separated as a brilliant crust of nodules of small prisms. Two different specimens were analysed: (i) crystallised from acetone and (ii) from ether [Found: (i) C, 74·9; H, 7·0; N, 8·3. (ii) C, 74·8; H, 7·1. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·1; N, 8·3%]. *Dihydrostrychnine* (*B*), m. p. about 196°, is somewhat soluble in water, yielding a bitter solution which on concentration deposits the substance in microscopic prisms. It dissolves readily in methyl alcohol or acetone and separates from the latter, often as twin crystals, in glistening prisms. The solution in dilute sulphuric acid (60%) gives with dichromate an intense bluish-purple coloration changing to green and then to brown and, on warming, to brownish-crimson, a reaction reminiscent of the behaviour of strychnine itself. Most specimens of this substance give a pale pink coloration when ferric chloride is added to their solutions in very dilute hydrochloric acid, but when the base is perfectly pure this reaction is negative, even on heating. Similarly the pure base does not couple with diazobenzenesulphonic acid. It is very readily soluble in dilute mineral acids and even in dilute acetic acid and is precipitated by ammonia

as a gum which, on warming and rubbing, crystallises. The *hydrochloride* is rather sparingly soluble and separates well as a voluminous mass of minute needles. When a boiling solution of this salt is mixed with a little sulphurous acid and excess of sodium iodide added, the *hydriodide* separates as a mass of glistening plates. It is sparingly soluble in acetone or methyl alcohol or in boiling water and separates from the last in glistening feathery groups which become opaque at 100°. It melts at 350—355° to a dark brown syrup (Found: C, 53·9; H, 5·5. $C_{21}H_{24}O_2N_2$,HI requires C, 54·3; H, 5·4%).

The methiodide. A solution of the base in boiling acetone gave, with methyl iodide, an immediate voluminous precipitate; this separated from methyl alcohol, in which it was sparingly soluble, in pale yellow feathery needles which changed partly to pale yellow prisms and, on recrystallisation, became needles again. The crystals darkened gradually above 220° and melted at about 365° (decomp.) (Found: C, 55·6; H, 5·8. $C_{21}H_{24}O_2N_2$,MeI requires C, 55·3; H, 5·6%). This methiodide is sparingly soluble in cold water and rather readily on boiling and separates as a soft mass of minute needles.

The methochloride. When the methiodide was digested with water and silver chloride, and the filtrate evaporated, the *methochloride* was obtained as a crystalline mass, separating from methyl alcohol in soft needles which became opaque on standing in the air (Found: C, 67·8; H, 7·2. $C_{21}H_{24}O_2N_2$,MeCl requires C, 68·3; H, 7·0%). This methochloride, m. p. 370—375° (efferv.), is readily soluble in water; the solution gives no coloration with ferric chloride and a little hydrochloric acid in the cold. A solution in dilute sulphuric acid (60%) gives with dichromate a blue coloration rapidly changing to purple and then to brown.

The *methobromide* separated as a mass of needles when sodium bromide was added to a hot concentrated solution of the methochloride. It is readily soluble in warm water and separates from methyl alcohol, in which it is sparingly soluble, in needles, m. p. about 375° (decomp.) (Found: C, 61·6; H, 6·3. $C_{21}H_{24}O_2N_2$,MeBr requires C, 61·3; H, 6·3%).

The *benzylidene* derivative was readily formed when a solution of the base (1 g.) in a little boiling alcohol was mixed with benzaldehyde (2 c.c.) and a few drops of concentrated sodium ethoxide and left for 2 days. On vigorous rubbing, crystallisation set in and, after being washed with water, the benzylidene derivative was recrystallised from methyl alcohol, in which it was very sparingly soluble, separating in glistening, pale lemon-yellow flitters, m. p. 270—275° (Found: C, 79·3; H, 6·5; N, 6·6. $C_{28}H_{28}O_2N_2$ requires C, 79·3; H, 6·6; N, 6·6%).

When the benzylidene derivative is moistened with hydrochloric acid the hydrochloride separates as a white powder, which is sparingly soluble in cold water but dissolves on boiling; the solution on cooling sets to a jelly. Ferric chloride added to an aqueous solution gives no coloration in the cold but a deep yellow on boiling. The sulphate is more soluble and the solution in 60% sulphuric acid gives, with dichromate, an intense blue colour changing to purple and then to brown. With 10% sulphuric acid this colour reaction is not shown.

Dihydrostrychnine (B) does not appear to yield an oxime, since on adding excess of hydroxylamine hydrochloride and some potassium carbonate to a solution in methyl alcohol and leaving the mixture for 24 hours, the base was recovered on dilution with water and extraction with ether and had m. p. 189—191° (Found: N, 8·0%).

The manganese precipitate (p. 981), from which the dihydrostrychnine (B) had been extracted with acetone, was extracted with boiling water and the brown extract was nearly neutralised with hydrochloric acid, concentrated by distillation under reduced pressure, and acidified; a considerable precipitate of a chocolate-coloured acid then separated which was washed with water and dried in a desiccator. The well-dried acid was extracted for some days in a Soxhlet apparatus with dry ether; from the extract, a small quantity of a pale yellow microcrystalline *acid* separated; this was soluble in boiling water, from which it crystallised rather indefinitely on cooling (Found: C, 60·2; H, 5·9; N, 7·0. $C_{21}H_{24}O_7N_2$ requires C, 60·6; H, 5·8; N, 6·7%). This acid froths and decomposes at about 205°, is readily soluble in dilute ammonia solution and in dilute sulphuric acid. A solution in 60% sulphuric acid gives with dichromate a fine bluish-purple coloration changing to purple and then to brown. Unfortunately, the amount of this acid available was so small that further investigation was impossible.

Hydrolysis of Dihydrostrychnine (B).—This substance was boiled with dilute methyl-alcoholic potassium hydroxide for several minutes without any apparent change and was precipitated on the addition of water, but when a solution of 1 g. in a little alcohol was heated in a sealed tube with sodium ethoxide (0·5 g. Na) in a boiling water-bath for 5 hours, complete hydrolysis occurred. The colourless solution was mixed with water and left over sulphuric acid in a vacuum; it then dried to a gum which was very readily and completely soluble in a little water. When this solution was acidified with hydrochloric acid and left over sulphuric acid, groups of feathery crystals containing chlorine gradually separated; these were recrystallised from dilute hydrochloric acid and dried first over sulphuric acid in a vacuum and then for a short time at 100° (Found:

C, 64·2; H, 6·7. $C_{21}H_{26}O_3N_2$,HCl requires C, 64·5; H, 6·9%). This *hydrochloride* of *dihydrostrychnic acid* (*B*) dissolves in concentrated nitric acid to an orange solution; on warming, a pale yellow crystalline substance separates which is readily soluble in hot water. The hydrochloride is very readily soluble in hot water : when ammonia is added to the cold solution there is no precipitate, but when the solution is boiled in a test-tube so that most of the ammonia escapes, a crystalline precipitate of the acid separates, the ammonium salt evidently being dissociated. The precipitate is washed with a little water and dried at 100° (Found : C, 70·7; H, 7·4. $C_{21}H_{26}O_3N_2$ requires C, 71·1; H, 7·3%). *Dihydrostrychnic acid* (*B*) melts at about 285° with effervescence and formation of dihydrostrychnine (*B*) (see below). A solution in dilute sulphuric acid (50%) gives a reddish-brown colour with dichromate, and addition of ferric chloride to a solution in very dilute hydrochloric acid gives no coloration in the cold but, on boiling, a deep brown-crimson colour develops. *Action of heat.* When a small quantity of the acid was cautiously heated in a test-tube, it effervesced and water was eliminated. The residue was ground and extracted with much boiling ether, and the ethereal solution concentrated to a small bulk and left; a pale yellow substance then separated in minute prisms, m. p. 203°. This substance, which gave an intense blue colour, changing to purple, when its solution in dilute sulphuric acid (50%) was mixed with dichromate, proved to be dihydro-strychnine (B), since a mixture with this substance melted at 201–202°. This method of formation is the only way, so far observed of raising the melting point of this substance from 196° to 203°.

Action of Perhydrol on Dihydrostrychnine (*B*).—The substance (0·5 g.), dissolved in methyl alcohol (15 c.c.), was mixed with methyl alcoholic potassium hydroxide (15 c.c.), and perhydrol (1 c.c. added. After 24 hours, the solution was concentrated to a small bulk, made acid to Congo-red with dilute hydrochloric acid, and left in the ice-chest. The clear solution gradually deposited a colourless crystalline substance which was washed with water and dried 100° (Found : C, 62·8; H, 6·7; N, 6·7. $C_{21}H_{26}O_6N_2$ requires 62·7; H, 6·5; N, 7·0%).

Dioxydihydrostrychnic acid becomes pale brown at 250°, da brown at 275°, and decomposes at 300—305° to a black mass. is rather sparingly soluble in cold water but dissolves readily boiling and separates as a crust of glistening pearly plates. solution in dilute sulphuric acid (50%) gives with dichromate orange coloration, deepening on warming; a solution in dil hydrochloric acid gives no coloration with ferric chloride.

Oxidation of Dihydrostrychnidine (*A*) (Part VI, J., 1927, 23

Formation of Oxydihydrostrychnidine (*A*).—Dihydrostrychnidine (A) (8 g.), dissolved in hot acetone (500 c.c.) and water (5 c.c.), was heated to boiling, and finely powdered permanganate added in small quantities at a time with frequent shaking. When 40 g. had been reduced, the liquid was filtered hot and the manganese precipitate extracted twice with boiling acetone. After distillation of some of the acetone on the steam-bath, the concentrated solution began to deposit crystals. When cold these (1·5 g.) were collected, washed with acetone, and crystallised from much boiling alcohol, from which the substance separated as a satiny mass of needles. More of the same substance was obtained by evaporating the acetone mother-liquors to dryness and rubbing the residual gum with methyl alcohol (Found: C, 74·8; H, 7·2; N, 8·4. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·1; N, 8·3%). *Oxydihydrostrychnidine* (*A*), isomeric with dihydrostrychnine (B) (m. p. 196°; p. 981), melts at about 345° to a black mass and is very sparingly soluble in most of the usual solvents. It dissolves in concentrated sulphuric acid without colour. A solution in 60% sulphuric acid gives with dichromate an immediate intense crimson colour, whereas the isomeride (B) gives a deep blue colour under the same conditions. It may be noted, however, that the final mother-liquors from the purification of the substance (A) contain a substance which also gives a deep blue colour with sulphuric acid and dichromate. Oxydihydrostrychnidine (A) is a feeble base, dissolving with difficulty in dilute hydrochloric acid. It is sparingly soluble in, and does not appear to combine with, methyl iodide, because when heated with a large excess of methyl iodide in a sealed tube in the water-bath for 2 hours it does not dissolve and the recovered substance, after being washed with methyl alcohol, melts at 336—340° and does not contain iodine. When an alcoholic solution of the base is heated in a sealed tube with benzaldehyde and a little sodium ethoxide there is no evidence of the formation of a benzylidene derivative.

In view of the feebly basic character of this substance and its non-identity with dihydrostrychnine (A), it is feasible to regard it as an *epi*dihydrostrychnine derived from dihydrostrychnidine (A) by the transformation of the group >N(*b*)·CH_2– into >N(*b*)·CO– (compare J., 1928, 3087, 3090).

Methoxymethyltetrahydrostrychnidine (*B*), $C_{23}H_{32}O_2N_2$, *Methyl-ψ-strychnidine* (*B*), $C_{22}H_{28}ON_2$, *and Dihydrostrychnidine* (*C*), $C_{21}H_{26}ON_2$.—These substances are obtained when dihydrostrychnidine (B) dimethochlorides or monomethochlorides are decomposed by methyl-alcoholic potash. (i) Crude dihydrostrychnidine dimethiodide (50 g.) (p. 977) is converted into the dimethochloride by digestion with water and silver chloride, the solution evaporated to dryness,

and the syrup dissolved in boiling methyl alcohol (100 c.c.). Methyl-alcoholic potash (300 c.c. of 25%) is added, and the whole heated on the steam-bath in an open flask for ½ hour. The flask is then transferred to a sand-bath, a thermometer inserted, and the heating continued until the temperature reaches 120°; there is then much frothing and, on removal of the flame, the temperature remains at this point for several minutes. Finally the whole is heated at 140—145° for about 15 minutes until effervescence has ceased. (ii) Dihydrostrychnidine (B) monomethochloride, obtained from the crude monomethiodide (p. 979) (50 g.) by digestion with silver chloride and evaporation to dryness, is digested with methyl-alcoholic potash (300 c.c.) exactly as described above. This process, although rather more tedious from start to finish, appears to proceed more smoothly and to give a purer product in better yield than (i). In either case, the cold product is mixed with crushed ice, water added, and the whole well shaken until the separation of the crude grey mass is complete. This is well washed, dried on porous porcelain, and dissolved in the minimum of boiling methyl alcohol, in which it is rather sparingly soluble, and filtered. The first crop, which separates rapidly on cooling and shaking, is collected and washed with methyl alcohol; the colourless crystalline mass is then usually almost pure *methoxymethyltetrahydrostrychnidine (B)*, m. p. 177—179°. When the filtrate is concentrated to about a quarter of its volume, a small second crop of the same substance separates, m. p. 165—172°. The mother-liquor is evaporated to dryness, and the residue dissolved in a little boiling acetone; on standing in the ice-chest, a further crop of nearly pure substance, m. p. 172—177°, separates. Finally, the filtrate is boiled for some hours with norite systematically concentrated, and left in the ice-chest with frequent rubbing until no further separation of a crystalline mass, m. p. 110—130°, consisting of crude *dihydrostrychnidine (C)* (p. 995) occurs. The treatment of the final mother-liquors is described on p. 994.

It is very important in carrying out the decompositions (i) and (ii) with methyl-alcoholic potash to be sure that the process is complete, otherwise serious loss may occur. In successful operation the yields of methoxymethyltetrahydrostrychnidine (B) and crude dihydrostrychnidine (C) are in (i) 22—25 g. and 2·3 g. and in (ii) 27 g. and 3—4 g., respectively, or roughly 70—75% of the theoretical. The final mother-liquors are added to the fraction, b. p. 215—220°/1 mm., mentioned below.

Considerable quantities of methoxymethyltetrahydrostrychnidine (B) were obtained from the brown mother-liquors from which dihydrostrychnidine dimethiodide had separated (p. 978). Wat

was added, the methyl alcohol removed on the steam-bath, and the hot liquid filtered from much tar and heated with excess of silver chloride. The filtrate, evaporated to a syrup, was mixed with a large excess of methyl-alcoholic potash and heated at 120—130° exactly as described above. The gum obtained on addition of water was dissolved in ether, the ethereal solution well washed, dried over potassium carbonate, and evaporated, and the dark brown syrup rapidly fractionated three times. The fraction, b. p. 215—225°/1 mm., when dissolved in methyl alcohol and rubbed, gradually *deposited a considerable quantity of crude methoxymethyltetra*hydrostrychnidine. The mother-liquor, when evaporated and distilled again, gave a pale yellow syrup, b. p. 220—225°/1 mm., which, dissolved in a little acetone and left for some weeks in the *ice-chest, deposited a material (5 g.) which softened at 155°* and was not completely melted at 190°. The separation of this into methoxymethyltetrahydrostrychnidine and *methylstrychnidine* (*B*), m. p. 223—225°, is described on p. 994.

Methoxymethyltetrahydrostrychnidine (*B*), like its isomeride (A), m. p. 220° (J., 1927, 1617), is remarkably sparingly soluble in ether or cold methyl alcohol and crystallises from the latter with great facility in colourless glistening needles, m. p. 179—180° (Found: C, 75·3, 75·0; H, 8·7, 8·6; N, 7·6; MeO, 8·0; Me as >NMe, 4·5; Me as combined Me, 8·4. $C_{23}H_{32}O_2N_2$ requires C, 75·0; H, 8·7; N, 7·6; MeO, 8·2; Me as >NMe, 4·1; 2Me as combined Me, 8·2%). It is very sparingly soluble in cold acetone, but dissolves moderately readily on boiling and separates beautifully in glistening triangular prisms; it also separates well from petroleum in glistening plates. When heated rapidly in small quantities in a test-tube, it distils largely unchanged; the distillate separates from methyl alcohol in plates, m. p. 178°. A moist acetone solution decolorises permanganate only slowly in the cold, but more readily on warming (p. 991). A solution in dilute sulphuric acid, on addition of a drop of dichromate, gives in the cold a crimson colour, which becomes very intense on warming. A solution in very dilute hydrochloric acid gives, with ferric chloride, no colour at first; a pink colour then gradually develops and becomes crimson on warming. The base dissolves to a bright red solution in concentrated nitric acid.

When the base was boiled with dilute sulphuric acid (10% by vol.) for 2 hours there was no sign of elimination of methyl alcohol and on addition of ammonia a thick curdy precipitate was produced which soon hardened; this separated from methyl alcohol in plates, m. p. 178°, and proved to be the unchanged base, practically the whole being recovered. In order to determine whether the substance was capable of electrolytic reduction, 1 g., dissolved in

dilute sulphuric acid (100 c.c. of 10% by vol.), was placed in the cathode chamber of the apparatus described in Part II of this research (J., 1924, **125**, 1798) and exposed for 14 hours to a current of 5 amps. at 22°. No reduction occurred, since the filtered solution gave, with ammonia, a solid base, m. p. 170—175°, which, after crystallisation from methyl alcohol, had m. p. 178—180°, almost the whole quantity being recovered.

The *hydriodide* was obtained by dissolving the base in a slight excess of dilute sulphuric acid and adding a few drops of concentrated sulphurous acid and then excess of sodium iodide. When the clear solution was warmed on the steam-bath, the crystalline canary-yellow hydriodide largely separated: after being well washed and dried on the steam-bath, this became colourless at 155—160°, softened and decomposed at 175—180°, solidified immediately, effervesced again at 235°, became again solid, and finally decomposed at about 325° to a brown froth (Found in substance dried at 105°: C, 56·0; H, 6·7. $C_{23}H_{32}O_2N_2$,HI requires C, 55·7; H, 6·6%). It is rather readily soluble in boiling water to a colourless solution and separates, on cooling slowly, in well-developed prisms. The mother-liquor from the canary precipitate gave with ammonia a considerable precipitate of the base.

The hydriodide was heated gradually in a test-tube in a sulphuric acid bath; methyl alcohol was eliminated at 250—260° and after about 10 minutes' heating at 260° decomposition was complete. The brittle grey mass was boiled with water; the filtered solution gradually deposited long, pale pink needles, but sometimes a jelly separated first which soon passed into the needles. The substance was recrystallised from water and dried at 100° (Found: C, 57·5; H, 6·2; N, 5·9. Calc. for $C_{22}H_{29}ON_2I$: C, 56·9; H, 6·3; N, 6·0%). That this substance, which melted at about 345° (decomp.), was a methiodide was shown by the fact that its aqueous solution gave no precipitate with ammonia or caustic potash even on warming, and that it was dihydrostrychnidine (B) methiodide (a) (p. 975) was demonstrated in the following way. The substance yielded the chloroform additive derivative characteristic of this methiodide, and when the methiodide was converted into the methochloride and this decomposed by heating in a test-tube, a yellowish-brown liquid remained which, distilled under 1 mm., dissolved in a little ether, and left in the ice-chest, gradually deposited crystals, m. p. 146—148° (Found: C, 78·0; H, 8·1; N, 8·4. Calc. for $C_{21}H_{28}ON_2$: C, 78·2; H, 8·1; N, 8·7%). That this substance was dihydrostrychnidine (B) was confirmed by the method of mixed melting point.

The same interesting change from methoxymethyltetrahydro-

strychnidine (B) to the methiodide of dihydrostrychnidine (B) takes place much more readily and completely when the base (1 g.) is boiled with hydriodic acid (5 c.c.; *d* 1·94) and a little amorphous phosphorus for 2 hours. The *solution is diluted with water* and filtered, and addition of excess of caustic potash then precipitates a gelatinous mass which separates from boiling water in needles, m. p. 345° (decomp.), and consists of the methiodide (a) of dihydrostrychnidine (B), the yield being almost quantitative.

The methiodide. Methoxymethyltetrahydrostrychnidine (B) (2 g.) is sealed up with methyl iodide (5 c.c.): there is little action in the cold but, on heating in the water-bath, a pale solution is formed which gradually becomes brown owing to the liberation of traces of iodine. After 2 hours there may be no separation, but if a crystal nucleus happens to be formed the whole quickly becomes a mass of crystals. If this is not the case, the methyl iodide is distilled off and the syrup is dissolved in a little hot methyl alcohol and well rubbed; crystallisation then soon sets in. The crystals are collected, washed with methyl alcohol, in which the *methiodide* is sparingly soluble, and dissolved in this medium, from which colourless, glistening, irregular, flat prisms separate; these become chalky at 110° and effervesce at 235—238° to a colourless liquid which crystallises at a higher temperature (Found in material dried at 110—115°: C, 56·5; H, 6·9. $C_{23}H_{32}O_2N_2$,MeI requires C, 56·5; H, 6·9%). This substance is sparingly soluble in cold but readily soluble in hot water, forming a supersaturated solution from which the methiodide separates in long striated prisms on the introduction of a crystal. It dissolves readily in cold chloroform and on leaving or warming there is no separation of an additive derivative.

Action of heat. The methiodide (3·22 g.) lost 0·91 g. of methyl iodide on heating at 250°, or 28·2% (calc. for $C_{23}H_{32}O_2N_2$,MeI losing MeI, 27·8%). The slight sublimate which formed melted at 178° and the residue separated from acetone in prisms, m. p. 178—180°, of pure methoxymethyltetrahydrostrychnidine (B).

The *methochloride*, obtained by digesting the methiodide with water and silver chloride for 2 hours, evaporating the solution to a small bulk, and placing it over sulphuric acid in a vacuum desiccator, separated in soft pearly crusts, which were left on porous porcelain and dried at 100° (Found: C, 68·7; H, 8·5. $C_{23}H_{32}O_2N_2$,MeCl requires C, 68·8; H, 8·4%).

This methochloride begins to decompose at about 150° and effervesces vigorously at 170°; the residue crystallises and consists of methoxymethyltetrahydrostrychnidine (B). It is very soluble in water and the addition of a drop of hydrochloric acid and then ferric chloride gives no coloration in the cold but, on warming, a

deep crimson colour develops, fading to brown and then to yellow. A solution in dilute sulphuric acid gives, with dichromate, a yellow colour changing to pink and then to deep crimson. When caustic potash (50%) is added to an aqueous solution of the methochloride the whole sets to a crystalline mass; on warming on the steam-bath, a pale brown syrup floats, crystallises on cooling, and consists of the unchanged methochloride.

The dimethosulphate. The base (7 g.), dissolved in dry benzene (50 c.c.), was mixed with freshly distilled methyl sulphate (20 c.c.) and heated under reflux on the steam-bath; after about 40 minutes, a gum commenced to separate which gradually changed to colourless prisms. After 2 hours, the deposit was collected, washed with benzene, dried on the steam-bath, and immediately analysed because the substance was deliquescent (Found: C, 52·0; H, 7·1. $C_{23}H_{32}O_2N_2,2Me_2SO_4$ requires C, 52·2; H, 7·1%). A solution in dilute sulphuric acid, on addition of dichromate, gives a yellow coloration which becomes deeper on warming. An aqueous solution mixed with ferric chloride and a little hydrochloric acid is coloured merely yellow but on boiling changes to bright green.

The dimethiodide. A solution of the dimethosulphate in hot water, when mixed with sodium iodide, gives a clear solution, which does not crystallise on rubbing and standing for 12 hours. The addition of caustic potash (50%) causes a caseous sticky precipitate to separate which soon hardens, and becomes crystalline on boiling with methyl alcohol. The substance crystallised from methyl alcohol, in which it was very sparingly soluble, in circular nodules which softened at about 205° and melted at 210°, becoming solid again. This dimethiodide is very readily soluble in cold water (Found in material dried at 110°: C, 45·9; H, 6·0. $C_{23}H_{32}O_2N_2,2MeI$ requires C, 46·0; H, 5·8%). The mother-liquors appeared to contain an isomeric dimethiodide, which was not isolated in a pure condition.

When the dimethiodide, m. p. 205—210°, was mixed with methyl-alcoholic potash (25%) and heated on the steam-bath, it did not dissolve but changed in appearance and the pasty liquid deposited a colourless crust. This was collected, washed with a little water, in which the substance was now sparingly soluble, and twice crystallised from methyl alcohol, separating as a soft mass of needles (Found in material dried at 100°: C, 56·2; H, 6·9. Calc. for $C_{23}H_{32}O_2N_2,MeI$: C, 56·5; H, 6·9%). Careful examination showed that this substance, m. p. 233—236° (efferv.), is identical with the methiodide obtained by the direct action of methyl iodide on methoxymethyltetrahydrostrychnidine (B) (see above).

Methoxymethyltetrahydrostrychnidine (B) dissolves in nearly

boiling benzyl chloride apparently without combination, since th solution, when diluted with ether, deposits the unchanged base The same is also true of the isomeride of m. p. 220° (J., 1927 1617).

Methoxybenzyltetrahydrostrychnidine (*B*).—Dihydrostrychnidin (B) benzylchloride (p. 981) (12 g.) was mixed with methyl-alcoholi potassium hydroxide (200 c.c. of 25%) and gradually heated on sand-bath until a thermometer placed in the melt registered 150 the decomposition proceeding very smoothly and without dis coloration. On addition of water to the cold mass, a colourless bas separated in almost quantitative yield; it was well washed an dissolved in ether, in which it was very soluble. The ethereal solu tion, dried over potassium carbonate and concentrated, did nc deposit crystals when kept in the ice-chest, as so readily happens i the case of methoxymethyltetrahydrostrychuidine (B) (p. 985 When, however, the ether was distilled off and the gum dissolved i methyl alcohol and rubbed, crystallisation rapidly set in and th colourless crystalline substance was now comparatively sparingl soluble in methyl alcohol and separated as a feathery mass (needles, m. p. 126—127° (Found: C, 78·9; H, 8·2; MeO, 6· $C_{29}H_{34}O_2N_2$ containing 1 MeO requires C, 78·7; H, 7·8; MeO 7·0%). It is very soluble in methyl iodide: when the solution boiled for a few minutes and the methyl iodide evaporated, a gu remains which on warming with water deposits the unchanged bas no combination having occurred under these conditions.

Formylmethoxytetrahydrostrychnidine (*B*) (p. 969).—This sub stance is obtained when methoxymethyltetrahydrostrychnidi (B), dissolved in moist acetone, is oxidised by permanganate. Th base (11 g.), dissolved in acetone (650 c.c.) and water (10 c.c.), wa mixed with very finely powdered permanganate (4 g.), the who being well shaken from time to time and the temperature kept 12°. After 24 hours, decolorisation was nearly complete an further quantities of the permanganate were gradually added unt when 14 g. had been added, decolorisation became extremely slo Five such lots were combined and heated for some minutes on th steam-bath, the manganese precipitate was well washed with aceton and the yellow filtrate and washings were concentrated to a sma bulk and left in the ice-chest for several days; the solution th either became a pasty mass of crystals or deposited a hard cru The crystals were collected, boiled with a little ether to remove gummy impurity, and fractionally crystallised several times fro methyl alcohol to remove the last traces of unchanged methox methyltetrahydrostrychnidine (B). The treatment of the lar amount of the oxidation product contained in the acetone and meth

ılcohol mother-liquors is described on p. 993. *Formylmethoxy-etrahydrostrychnidine* (*B*) separates from methyl alcohol in brilliant, ;olourless, well-developed prisms, which rapidly become opaque vhen exposed to the air on a watch glass (Found: C, 72·0; H, 7·9; N, 7·3; MeO, 8·0; >NMe, none. $C_{23}H_{30}O_3N_2$ containing 1 MeO equires C, 72·3; H, 7·8; N, 7·3; MeO, 8·1%). It melts at 154°, s very soluble in hot, but much less so in cold, methyl alcohol, and s almost insoluble in boiling water. Dichromate added to a solution f the formyl derivative in dilute sulphuric acid gives a yellow oloration, quickly changing to pink and becoming crimson on varming. A solution in very dilute hydrochloric acid is coloured ellow by ferric chloride, but gradually an intense crimson colour evelops which is not destroyed by excess of hydrochloric acid. 'he base dissolves in concentrated nitric acid to a deep yellow olution. In order to see whether it was capable of hydrolysis, the ase was heated with alcoholic sodium ethoxide in a sealed tube in he water-bath for 2 hours. On addition of water the solution ecame turbid, and when the alcohol was evaporated a syrup eparated which crystallised from methyl alcohol, had m. p. 152—54°, and consisted of the unchanged substance. On treatment ith benzaldehyde and sodium methoxide in methyl-alcoholic olution, the base is not converted into a benzylidene derivative. he base is readily soluble in, but does not appear to combine with, ıethyl iodide, since in two experiments in which it was heated) with methyl iodide and methyl alcohol in a sealed tube for ½ hour, nd (ii) for the same time with methyl iodide alone, practically the hole of it was recovered unchanged.

Action of Dilute Sulphuric Acid on Formylmethoxytetrahydro-rychnidine (*B*). *Formation of Methoxytetrahydrostrychnidine* (*B*).—his interesting decomposition was brought about (1) by boiling rmylmethoxytetrahydrostrychnidine (B) with dilute sulphuric id, and (2) by distilling this substance under reduced pressure ee below). (1) Formylmethoxytetrahydrostrychnidine (B) (1 g.), ssolved in dilute sulphuric acid (20 c.c. of 10% by vol.), was oiled under reflux for an hour, the cold product mixed with excess potassium hydroxide, and the cloudy solution extracted twice ith ether. The ethereal solution was dried over potassium car-onate, concentrated to a small bulk, cooled, and rubbed; crystal-ıation soon commenced and, after the mixture had been kept for me hours in the ice-chest, the solid was collected, washed with her, and crystallised from this solvent. The colourless leaflets otained became opaque on the steam-bath, melted at 150—152°, ıd were not identical with the original base (m. p. 154°), because a ixture of the two softened at 123° and was nearly melted at 130°

(Found : C, 74·3, 74·4; H, 8·5, 8·4; N,7·8; MeO, 8·0. $C_{22}H_{30}O_2N_2$ containing 1 MeO requires C, 74·6; H, 8·5; N, 7·9; MeO, 8·7%).

Methoxytetrahydrostrychnidine (*B*) dissolves in dilute sulphuric acid (60%) to a pale pink solution which becomes crimson on the addition of dichromate. A solution in very dilute hydrochloric acid gives no immediate coloration with ferric chloride, but a pink colour rapidly develops. A crystal of the base dissolves in concentrated nitric acid to a deep salmon solution. The *nitroso*-derivative separated, when sodium nitrite was added to a well-cooled solution of the base in very dilute hydrochloric acid, as a light yellow, crystalline mass; after addition of sodium acetate, the precipitate was collected, washed, and dried over sulphuric acid in a vacuum desiccator [Found : N, 10·7. $C_{22}H_{29}(NO)O_2N_2$ requires N, 11·0%].

In order to determine whether the methoxy-base was susceptible to electrolytic reduction a solution of 1 g. in 30 c.c. of 15% sulphuric acid was placed in the usual electrolytic reduction apparatus (J., 1924, **125**, 1798) and subjected to a current of 4 amps. for 20 hours. The colourless solution was diluted with water and made alkaline with potassium hydroxide, the milky liquid extracted with ether, and the extract dried over potassium carbonate, concentrated, and kept in the ice-chest; pearly plates separated which melted at 149—151° and consisted of the unchanged base (Found : C, 74·2; H, 8·4%).

Action of methyl iodide. The base dissolved readily in methyl iodide with some rise of temperature, crystals gradually separated, and increased in quantity on heating in a sealed tube in the water-bath. After 2 hours the excess of methyl iodide was distilled off and the crystals were dissolved in boiling methyl alcohol; they separated again as a pale yellow crust, which became opaque on the steam-bath and then melted at about 235° (efferv.), became solid again, and finally decomposed at 320—325° (Found: C, 55·2; H, 6·6. Calc. for $C_{23}H_{32}O_2N_2$,HI: C, 55·7; H, 6·6%). It is explained on p. 969 that this substance is the hydriodide of methoxymethyltetrahydrostrychnidine (B) (compare p. 988). It dissolves readily in warm water and on addition of ammonia colourless crystals immediately separate which crystallise from methyl alcohol in glistening flitters, m. p. 178—180° : there is no depression on admixture with an equal quantity of methoxymethyltetrahydrostrychnidine (B).

Distillation of Crude Formylmethoxytetrahydrostrychnidine (*B*).—Results at first difficult to understand were obtained when the acetone and methyl-alcoholic mother-liquors from a number of preparations of this substance, m. p. 154° (p. 991), were evaporated and distilled. After a good deal of frothing and decomposition,

about two-thirds distilled at 225—265°/1 mm., leaving a dark tar, and after two more fractionations most of the substance passed over at 218—223°/1 mm. and set to a pale amber resin (22 g.) on cooling. This was readily soluble in ether : the concentrated cooled solution, from which a mass of crystals began to separate almost immediately, was kept for some days in the ice-chest; the mass then consisted of hard nodules covered with soft needles. By shaking with ether and rapid decantation, the needles were easily separated from the nodules; after recrystallisation they had m. p. 152—154° and consisted of formylmethoxytetrahydrostrychnidine (B) which had escaped decomposition during the distillation. This was proved by analysis (Found : C, 72·1; H, 7·8; N, 7·3. Calc. for $C_{23}H_{30}O_3N_2$: C, 72·3; H, 7·8; N, 7·3%) and by the method of mixed melting point. The nodules had m. p. 130—135° and after many recrystallisations from ether, in which the *substance* was readily soluble, the m. p. rose to 137—138° (Found : C, 74·2; H, 8·2; MeO, 8·2. $C_{22}H_{30}O_2N_2$ *containing* 1 MeO *requires* C, 74·6; H, 8·5; MeO, 8·7%). This analysis and the fact that the melting point could not be raised above 137° by recrystallisation seemed to indicate that the substance was a second modification of methoxytetrahydrostrychnidine (B) (m. p. 154°). This view received support from the fact that the nodules, on treatment with methyl iodide, also yielded the hydriodide of methoxymethyltetrahydrostrychnidine (B) (see above). When, however, the nodules were boiled with dilute sulphuric acid and the base was set free with alkali, the crystalline mass no longer separated in nodules but in needles, which melted at 150—152° and at the same temperature when mixed with methoxytetrahydrostrychnidine (B), m. p. 152°. It seems probable, therefore, that the nodules consist of this substance contaminated with small quantities of formylmethoxytetrahydrostrychnidine (B) (m. p. 154°) which resist separation by crystallisation but are converted into methoxytetrahydrostrychnidine (B) (m. p. 152°) by boiling with dilute sulphuric acid.

Methyl-ψ-strychnidine (*B*) *and Dihydrostrychnidine* (*C*).—The final acetone and methyl-alcoholic mother-liquors collected from the purification of a large number of preparations of methoxymethyltetrahydrostrychnidine (B), and from which crude dihydrostrychnidine (C) had separated (compare p. 986), were evaporated and the gummy residue was distilled under reduced pressure, a considerable fraction passing over at 220—225°/1 mm. This was dissolved in acetone and left in the ice-chest in contact with a crystal of methoxymethyltetrahydrostrychnidine (B) for 2 weeks; a thin crust of this base, m. p. 165—175°, then separated. The filtrate, when concentrated and left for some months, deposited about 6 g.

of a substance, m. p. 185—210°; after several crystallisations from alcohol, in which the substance was very sparingly soluble, *methyl-ψ-strychnidine* (*B*) was obtained in brilliant needles, m. p. 222—225° (Found: C, 78·9; H, 8·0; N, 8·3; Me as >NMe, 4·5. $C_{22}H_{28}ON_2$ containing one >NMe requires C, 79·0; H, 7·8; N, 8·4; Me as >NMe, 4·5%).

A solution of methyl-ψ-strychnidine (B) in dilute sulphuric acid (60%) gives an intense crimson colour with dichromate, and addition of ferric chloride to a solution in very dilute hydrochloric acid also produces an immediate crimson colour.

The dimethiodide. The base combines with methyl iodide with some evolution of heat. The mixture was heated in a sealed tube for a few minutes in the water-bath, the excess of methyl iodide distilled off, and the residue dissolved in methyl alcohol. The solution remained for a long time, but, on rubbing, the *methiodide* gradually separated as a crust of minute needles, which melted at about 275° and effervesced vigorously at 280—285°, leaving a pale yellow syrup which crystallised (Found: C, 46·7; H, 5·6. $C_{22}H_{28}ON_2$,2MeI requires C, 46·6; H, 5·2%). The dimethiodide is somewhat sparingly soluble in cold water, moderately easily soluble in boiling water, and crystallises therefrom in minute needles. In attempting to prepare the dimethochloride, the following curious and characteristic behaviour was observed. When silver chloride was added to a boiling dilute aqueous solution of the methiodide, a pale pink colour developed which, on concentration of the filtered solution on the steam-bath, soon became purplish-pink and then deep purple; when kept over sulphuric acid in a vacuum, the whole dried up to a blackish-purple jelly.

Dihydrostrychnidine (*C*). The mother-liquors from the methyl-ψ-strychnidine (B) yielded, on concentration, a further small quantity of this substance. The filtrate, further concentrated and left in the ice-chest for some weeks, gradually deposited a considerable crop of crystals which proved to be a mixture of dihydrostrychnidine (C) with a little methoxymethyltetrahydrostrychnidine (B) (m. p. 180°). The solid was collected, dissolved together with the substance, m. p. 110—130°, obtained as described on p. 986, in a little acetone, and left in the ice-chest for several days; almost the whole of the substance, m. p. 180°, was deposited as a thin crust; when the mother-liquor was exposed to the air, groups of prisms separated. On repeated fractional crystallisation from ether this crude material yielded brilliant prisms of dihydrostrychnidine (C). These crystals were kindly examined by Dr. T. V. Barker, who reports that no diagrams are necessary, since the habit is simple and constant. The system is monoclinic, $a : b : c = 1{\cdot}037 : 1 : ?$; $\beta = 113° 48'$, the forms

developed being *c* (001) and *m* (110) of equal size and *a* (100) considerably smaller. Following are the results of measurement of two crystals:

	m(110).	*a*(100).	*c*(001).
ϕ	0° 0′	0° 0′	66° 12′
c	46° 31′	90° 0′	90° 0′

Optically an axis emerges through *m*, indicating the axial plane to be normal to *b* (010). The extinction on *m* is about 20° inclined to the vertical edge.

Owing to the fact that the melting point was never quite sharp, two specimens were analysed, namely, (*a*) the prisms from ether and (*b*) the needles from methyl alcohol (see below) [Found: (*a*) C, 78·3; H, 8·3; N, 8·4; Me as >NMe, none. (*b*) C, 78·1; H, 8·2. $C_{21}H_{26}ON_2$ free from >NMe requires C, 78·2; H, 8·1; N, 8·7%]. *Dihydrostrychnidine* (*C*) is readily soluble in ether or acetone but is much less soluble in methyl alcohol, from which it separates, when the solution is rapidly concentrated, in brilliant glistening needles, softening at about 128° and melting at 132—134°. It is a strong base, dissolving readily in dilute acetic acid. A solution in very dilute hydrochloric acid gives no immediate coloration with ferric chloride in the cold, but gradually a yellow colour develops which becomes brownish-pink and, on heating, pale brown. A solution in dilute sulphuric acid (60%) gives with dichromate approximately the same colour changes.

The base was heated with methyl iodide in the steam-bath for a few minutes; no crystallisation took place and on evaporation a gummy substance was obtained which consisted essentially of the monomethiodide. This was readily soluble in water and the solution gave no precipitate with caustic potash. When, however, a solution of the base (1 g.) in methyl iodide (2 c.c.) and methyl alcohol (2 c.c.) was heated in a sealed tube in the steam-bath no change was observed during 3—4 hours; a substance then began to separate in small prisms and the quantity increased slowly during 7 hours. After remaining over-night, the crystals were collected and dissolved in a little boiling water, from which the *dimethiodide* separated as a chalky crust of minute needles, m. p. 265—270°, effervescing to an amber resin (Found in material dried at 100°: C, 44·9; H, 5·2. $C_{21}H_{26}ON_2$,2MeI requires C, 45·5; H, 5·3%).

The dimethochloride, obtained by adding silver chloride to a hot aqueous solution of the dimethiodide and evaporating the filtered liquid, is a non-crystalline brittle mass very soluble in water. When this was heated with methyl-alcoholic potassium hydroxide until the temperature reached 150° (compare p. 985), decomposition took place smoothly and, on addition of ice-water to the cold mass, an

ochreous precipitate was obtained which separated from methyl alcohol in glistening plates, m. p. 127—129°, and consisted of dihydrostrychnidine (C), methyl chloride having been eliminated during the process. Identity was established by a mixed m. p. determination, by analysis (Found: C, 78·2; H, 8·3%) and by conversion into the dimethiodide, which was identical with the derivative described above.

In an attempt to reduce dihydrostrychnidine (C) electrolytically, the base (1 g.), dissolved in dilute sulphuric acid (40 c.c. of 10% by volume), was subjected in the usual electrolytic reduction apparatus (J., 1927, 1600) to a current of 5 amps. for 6 hours. The chalky precipitate which separated on addition of caustic potash was collected, dried, and recrystallised from methyl alcohol, separating in needles, m. p. 127—132° (Found: C, 78·0; H, 8·2%). That the substance was unchanged was confirmed by a mixed m. p. determination.

It is conceivable that crude dihydrostrychnidine (B) already contains this isomeride (C) and that the bases are stereoisomerides owing their origin to the new asymmetric carbon atom in a group $^-CHMe^-$ derived from $^-CH_2{\cdot}CH_2^-$ in strychnidine.

Benzylidenestrychnine.—As explained in the introduction (p. 966), we were led to attempt the condensation of strychnine and some of its simple derivatives with aromatic aldehydes as the result of a theoretical argument based on the properties of dihydrostrychnine (B). We find that strychnine and brucine and many of their derivatives, provided that these retain the group $>N(a){\cdot}CO^-$, condense readily with benzaldehyde, anisaldehyde, or piperonal and we are engaged in the detailed investigation of the new bases so obtained.

Owing to the readiness with which it is formed and its good crystallising power, benzylidenestrychnine is a highly characteristic derivative of the alkaloid, but it does not appear to have been previously described. Finely powdered strychnine (34 g.) was added to a boiling mixture of 94% alcohol (300 c.c.) and benzaldehyde (25 c.c.). On the introduction of a solution of potassium hydroxide (5 g.) in water (10 c.c.), the boiling being continued, the strychnine quickly dissolved, giving an orange-yellow solution. The source of heat was then removed and in a few seconds there was a copious separation of glistening yellow leaflets. After cooling, the derivative was collected, washed with alcohol, water, and alcohol, and dried at 100°. The base is very sparingly soluble in boiling alcohol or ethyl acetate, more readily soluble in hot toluene, acetone or pyridine; it may be conveniently crystallised from *iso*amyl alcohol, separating in pale lemon-yellow

leaflets, m. p. 235—237° (Found : C, 79·1, 79·9 *; H, 6·2, 6·4; N, 6·4. $C_{28}H_{26}O_2N_2$ requires C, 79·6; H, 6·2; N, 6·6%). *Benzylidenestrychnine* dissolves in concentrated hydrochloric acid to an intensely yellow solution and on dilution with water the colour is largely discharged and the sparingly soluble hydrochloride is precipitated. Its yellow solution in 60% sulphuric acid gives a deep pure blue coloration on the addition of dichromate; this becomes dull green and then brown on keeping. The substance readily forms a methosulphate and other derivatives which will be described subsequently.

In contrast, benzylidenebrucine crystallises with difficulty, but the characteristic *hydrochloride* is readily prepared in the following manner: Caustic potash (4 g.) in water (10 c.c.) is added to a boiling solution of brucine (20 g.) and benzaldehyde (10 c.c.) in alcohol (50 c.c.) contained in a large beaker. After 2 minutes' boiling, the product is cooled, mixed with ether and then with concentrated hydrochloric acid (20 c.c.) diluted with water (200 c.c.). The ether is poured off, fresh ether added, and then a crystal of the hydrochloride from a previous preparation; copious crystallisation of the hydrochloride of benzylidenebrucine occurs. After being washed with dilute hydrochloric acid, this separates from alcoholic hydrogen chloride (2%) in yellow needles which, dried at 100°, appear to contain $\frac{1}{2}H_2O$ (Found : C, 68·3; H, 6·4.

$$C_{30}H_{30}O_4N_2,HCl,\tfrac{1}{2}H_2O$$

requires C, 68·3; H, 6·1%).

We propose to submit this salt and the corresponding, readily soluble base to detailed examination.

Derivatives of Strychnidine.

Strychnidine Methosulphate, $C_{21}H_{24}ON_2,Me_2SO_4$.—The following modification of the method described in Part IV (J., 1927, 1600) gives excellent results and is convenient for the preparation of large quantities of the substance. Strychnidine (50 g.) is finely powdered and stirred in a mortar while a mixture of freshly distilled methyl sulphate (20 c.c.) and methyl alcohol (25 c.c.) is gradually added. Interaction takes place immediately and the whole sets to a hard mass, which is ground, washed with methyl alcohol, and dried at 100°.

Strychnidine Methochloride, $C_{21}H_{24}ON_2,MeCl$.—Strychnidine methiodide (Tafel, *Annalen*, 1898, **301**, 314), dissolved in hot water, was mixed with a large excess of freshly precipitated silver chloride and heated on the steam-bath for 3 hours. The filtrate from the silver salts was evaporated to a small bulk and left in the ice-chest.

* Lead chromate tube.

The *methochloride*, which separated as a voluminous mass of needles, was collected, washed with a little water, in which it was very soluble, and left on porous porcelain for 2 days (Found: loss at 100°, 8·2. Found in the dried material: C, 71·7; H, 7·4. $C_{22}H_{27}ON_2Cl,2H_2O$ requires H_2O, 8·8%. $C_{22}H_{27}ON_2Cl$ requires C, 71·3; H, 7·3%). It melts and decomposes at about 370°, leaving a residue containing strychnidine.

When an aqueous solution is dechlorinated by silver hydroxide, and the filtrate concentrated by distillation under reduced pressure and then over sulphuric acid, a colourless crystalline mass—presumably the methohydroxide—remains: this will be examined.

Strychnidine Dimethosulphate, $C_{21}H_{24}ON_2,2Me_2SO_4$.—Strychnidine (25 g.), suspended in dry benzene (200 c.c.), was heated to boiling and the clear solution obtained was cooled and rapidly mixed with methyl sulphate (40 c.c.) before crystallisation set in. When the viscid gelatinous mass of strychnidine methosulphate was heated on the steam-bath, the whole gradually became more limpid and after 20 hours a thick gum had separated below the benzene. The benzene layer was decanted, the gum washed with benzene, the benzene shaken with water, and the aqueous extract used to dissolve the gum. After being filtered from some benzene, the solution of the dimethosulphate was heated to boiling and nearly neutralised with potassium hydroxide, and a large excess of hot concentrated sodium iodide solution added: the clear liquid soon began to deposit a glistening colourless mass of *strychnidine dimethiodide*. This is sparingly soluble in cold water, much more readily on boiling, and separates in long brilliant needles (Found: C, 45·4; H, 5·2. $C_{21}H_{24}ON_2,2MeI$ requires C, 45·7; H, 5·0%).

The dimethochloride, prepared in the usual way from the dimethiodide and silver chloride, was deposited as a gum on evaporation of the aqueous solution. When heated with a large excess of methyl-alcoholic potassium hydroxide (25%) until the temperature rose to 140°, the gum was readily decomposed and on addition of water a grey mass was obtained which separated from methyl alcohol in colourless prisms, m. p. 125°, and was readily identified by analysis and by a mixed melting-point determination as methoxymethyldihydrostrychnidine (J., 1927, 1602). It is remarkable that the specimen obtained was much freer from purple colouring matter than the material prepared from strychnidine monomethosulphate under the same conditions.

Strychnidine Benzylchloride, $C_{21}H_{24}ON_2,C_7H_7Cl$.—A solution of strychnidine (20 g.) in boiling toluene was cooled somewhat, and benzyl chloride (12 c.c.) added: combination began at once with separation of crystals and the whole soon became a paste. The

mass was collected, washed with ether, and dissolved in boiling methyl alcohol, and the clear solution mixed with ether. The glistening plates which separated were washed with ether and dried at 100° (Found: C, 75·0; H, 6·9; Cl, 7·8. $C_{28}H_{31}ON_2Cl$ requires C, 75·2; H, 6·9; Cl, 8·0%).

Strychnidine benzylchloride, m. p. 330—335° (efferv.), is very soluble in water. The solution gives no precipitate with alkali, but with dichromate a sparingly soluble, bright yellow chromate is obtained. A solution in dilute sulphuric acid (60%) gives with dichromate the ordinary crimson strychnidine reaction. When the dry substance is heated in small quantities in test-tubes, benzyl chloride is eliminated and strychnidine regenerated, but at the same time small quantities of other substances are produced which are under examination.

When strychnidine benzylchloride (20 g.) is heated with methyl-alcoholic potash (250 c.c. of 25%) until the temperature of the melt reaches 150° and the whole is then cooled and water added, a solid separates in very good yield which is difficult to crystallise and melts at 92—95° (Found: C, 78·5; H, 7·7; MeO, 7·6. $C_{29}H_{34}O_2N_2$ requires C, 78·7; H, 7·7; MeO, 7·1%). This base, which is evidently *methoxybenzyldihydrostrychnidine* (compare Part IV, J., 1927, 1602), will be subjected to a detailed examination.

We are indebted to Mr. R. I. E. Hall, M.A., for the preparation of most of the dihydrostrychnidine (B) required for this investigation and to Mr. F. Hall for carrying out the analyses. We desire also to thank the Government Grant Committee of the Royal Society for repeated grants towards the heavy cost of the work.

THE DYSON PERRINS LABORATORY, OXFORD.

UNIVERSITY COLLEGE, LONDON.

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CXXIX.—*The Introduction of the Triphenylmethyl Group into Phenols. Part II.*

By DOUGLAS VERNON NELMAR HARDY.

IT has previously been shown that the Baeyer–Villiger reaction may be utilised in order to condense triphenylcarbinol with phenol and anisole (Baeyer and Villiger, *Ber.*, 1902, **35**, 3018), pyrocatechol (Zincke and Wugk, *Annalen*, 1908, **363**, 284), *o*-cresol, *o*-tolyl methyl ether, and *m*-cresol (Schorigin, *Ber.*, 1927, **60**, 2373; Part I, Boyd and Hardy, J., 1928, 630). Moreover, the failure of the

reaction has been observed with *p*-cresol (Schorigin, *loc. cit.*) and with methyl salicylate (Part I), but whereas the latter is quite unreactive, the former induces a novel reaction in which the triphenylcarbinol is reduced to triphenylmethane and the *p*-cresol is oxidised to a product for which the constitution of a highly polymerised *p*-quinomethane has been suggested. With a view to elucidate the factors which determine this variation in behaviour, an extended study of the Baeyer–Villiger reaction has been undertaken.

According to their behaviour towards an acetic–sulphuric acid solution of triphenylcarbinol, phenols and phenolic ethers fall naturally into three groups, *viz.*, those which undergo condensation (group I), those under whose influence the carbinol is reduced to triphenylmethane (group II), and those which are unreactive (group III).

Group I: Phenol, anisole, phenetole, *o*-cresol, *o*-tolyl methyl ether, *o*-tolyl ethyl ether, *m*-cresol, pyrocatechol, guaiacol, veratrole, resorcinol and its dimethyl ether, quinol, pyrogallol and its trimethyl ether, thymol, α- and β-naphthols, *o*-chlorophenol,* and *o*-bromophenol.*

Group II: *p*-Cresol, *p*-tolyl methyl and ethyl ethers, *o*-,* *m*-, and *p*-chlorophenols, *o*-bromophenol,* and quinol dimethyl ether.

Group III: *o*- and *p*-Nitrophenols, picric acid, *o*- and *p*-nitroanisoles, salicylic acid and its methyl ester, trichlorophenol, trichloroanisole, and tribromophenol.

The addition of any member of groups I and II to an acetic–sulphuric acid solution of triphenylcarbinol causes the production of a deep brown colour, but the members of group III produce no appreciable alteration in the reddish-orange colour of the carbinol solution. These and previous results permit three deductions, namely, (1) the deep brown colours indicate the formation of intermediate compounds, (2) the formation of these intermediate compounds is essential to reaction, and (3) the primary reaction takes place between the ions of triphenylmethyl sulphate (compare Part I) and the undissociated phenol—since the phenolic ethers react similarly to the phenols.

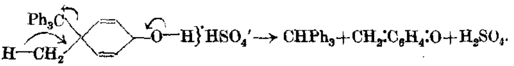
As applied to members of group I, the Baeyer–Villiger reaction serves, in general, to introduce one triphenylmethyl group into the nucleus, but, contrary to a statement by Schorigin (*Ber.*, 1928, **61**, 2517) that "Es tritt bekanntlich in den Kern eines Phenols stets nur ein Triphenylmethyl-Rest ein, . . ." di-triphenylmethylation has been observed with α-naphthol and with 1 : 3-dimethoxybenzene.

* In the reactions with *o*-chlorophenol and with *o*-bromophenol condensation and formation of triphenylmethane occur simultaneously.

The available data indicate that, although the triphenylmethyl group usually enters the nucleus para to hydroxyl, methoxyl, etc., ortho-substitution occasionally occurs.

Reaction with members of group II involves the oxidation of the phenol or phenolic ether, a process which in some cases can only be realised by removal of nuclear hydrogen and in others probably follows the lines indicated by the researches of Pummerer, Goldschmidt, Hunter, and others (see Davis and Hill, *J. Amer. Chem. Soc.*, 1929, **51**, 493). The oxidation products are usually intractable oils or resins, but from *p*-cresol two amorphous solids have been isolated, *viz.*, (A) a red substance of high melting point, believed to be a highly polymerised *p*-quinomethane, which was obtained by Schorigin (*loc. cit.*) on carrying out the reaction at 100°; and (B) a yellowish-brown substance of comparatively low melting point which has now been isolated by working at room temperature. It has been suggested that A is formed by the dehydration of *p*-toluquinol, a compound which, together with three amorphous substances, was isolated by Bamberger (*Ber.*, 1903, **36**, 2030) by oxidising *p*-cresol with Caro's acid. The properties of B are closely in agreement with those of one ($C_{14}H_{10}O_3$) of Bamberger's amorphous substances.

In Part I of this investigation, a mechanism of the Baeyer-Villiger reaction was suggested which, when generalised, assumes (i) nuclear attack by the triphenylmethyl kation, and (ii) that the formation of triphenylmethane is preceded by the elimination of the triphenylmethyl *anion* from the complex:

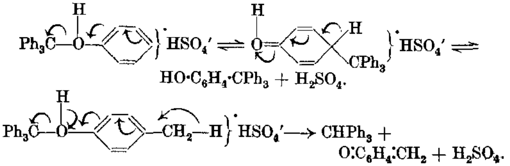


An alternative mechanism has been suggested by van Alphen (*Rec. trav. chim.*, 1927, **46**, 799) for the analogous reaction between triphenylmethyl chloride and phenol. This assumes the formation of an oxonium intermediate which, under the influence of an alkaline medium, *e.g.*, pyridine, loses hydrogen chloride to form phenyl triphenylmethyl ether (compare Helferich, *Ber.*, 1925, **58**, 882), whereas under acid conditions it undergoes intramolecular rearrangement, the triphenylmethyl group migrating to the *p*-position of the nucleus:

$$C_6H_5{\cdot}OHCl{\cdot}CPh_3 \longrightarrow Ph_3C{\cdot}C_6H_4{\cdot}OH(p) + HCl.$$

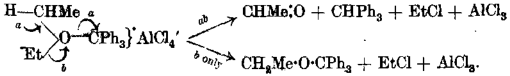
On these assumptions also must the triphenylmethyl anion play an essential part in the reaction, for not only must it be eliminated

prior to the formation of triphenylmethane, but it must, in addition, be the migrating group :

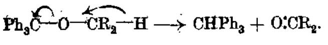


The available evidence is insufficient to decide between the two mechanisms, both of which provide an adequate explanation of the unreactivity of the members of group III, attributing it on the one hand to reduced nuclear reactivity and on the other to the inhibition of oxonium formation consequent upon increased acidity.

Contained in the literature are a number of reactions in which the triphenylmethyl anion would seem to be formed. Schmidlin (*Ber.*, 1912, **45**, 3180) observed the formation of 4-hydroxytetraphenylmethane and triphenylmethane by the action of phenol upon hexaphenylethane. It would appear highly probable that the hexaphenylethane dissociates into triphenylmethyl anions and kations, and whilst the latter attack the phenol, the former accept the subsequently expelled protons. Again, triphenylmethyl chloride has been shown to react with pure ether in presence of zinc chloride (Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 204) and of aluminium chloride (Norris and Young, *ibid.*, 1924, **46**, 2580) to give triphenylmethane and acetaldehyde. Evidence exists that ethyl triphenylmethyl ether may also be produced, a reaction which is included in the following scheme :



Norris and Young (*loc. cit.*) found also that alkyl triphenylmethyl ethers suffer thermal decomposition into triphenylmethane and the aldehyde or ketone corresponding to the alkyl group :



Preliminary experiments upon the introduction of other triarylmethyl groups into phenols have been carried out. These and allied investigations are being continued.

Experimental.

The Action of Triphenylcarbinol upon Phenols and Phenolic Ethers in the Presence of Sulphuric Acid.—Except where otherwise stated, the reaction mixtures were prepared by dissolving triphenylcarbinol (6 g.) and the phenol or phenolic ether (6 g.) in acetic acid (60 c.c.) by warming, and adding sulphuric acid (10 g.) to the warm solution.

(1) *Phenetole.* After standing for a week, the crystalline condensation product was collected, washed with dilute acetic acid, and dried (3·8 g.); a further quantity (2·58 g.) was obtained by diluting the mother-liquor. It was twice recrystallised from benzene–alcohol and then formed a colourless powder, m. p. 191° (Found : C, 88·7; H, 6·8. $C_{27}H_{24}O$ requires C, 89·0; H, 6·6%).

4-*Ethoxytetraphenylmethane* is difficultly soluble in acetic acid and in alcohol and easily soluble in benzene. When boiled with a mixture of acetic and hydriodic acids, it was converted into 4-hydroxytetraphenylmethane.

(2) *Pyrocatechol.* The 3 : 4-dihydroxytetraphenylmethane (8·10 g.) was collected after 10 minutes, washed, dried, and recrystallised from acetone or from toluene. It formed colourless needles which became brown at 260°, and melted at 262° as recorded by Zincke and Wugk (*loc. cit.*).

(3) *Guaiacol.* The washed (with alcohol) and dried product (8·2 g.), which was collected after 24 hours, was repeatedly crystallised from acetic acid and also from benzene–petrol, but a fraction of definite melting point could not be obtained. On boiling with a mixture of hydriodic and acetic acids it was converted into 3 : 4-dihydroxytetraphenylmethane, m. p. and mixed m. p. with an authentic specimen, 262°. The product consisted, therefore, of a mixture of 4-hydroxy-3-methoxy- and 3-hydroxy-4-methoxy-tetraphenylmethane.

(4) *Veratrole.* 7·62 G. of product were obtained as under (3) and consisted of almost pure 3 : 4-dimethoxytetraphenylmethane. Dilution of the reaction mixture furnished a further quantity. The substance formed colourless prisms, m. p. 170° after recrystallisation from acetic acid, as recorded by Gomberg and Forrester (*J. Amer. Chem. Soc.*, 1925, **47**, 2389) for the compound obtained by treating 3 : 4-dimethoxytriphenylmethyl chloride with magnesium phenyl bromide. By treatment with a mixture of hydriodic and acetic acids the substance was converted into 3 : 4-dihydroxytetraphenylmethane.

(5) *Resorcinol.* Sulphuric acid (5 g.) was added to a solution of triphenylcarbinol (4 g.) and resorcinol (4 g.) in acetic acid (30 c.c.) and as soon as the mixture was cold the crude 2 : 4-dihydroxytetra-

phenylmethane was collected, washed with alcohol, and dried (4·04 g.). After recrystallisation from toluene and then from acetone it formed colourless crystals, m. p. about 268° with previous shrinkage and decomposition. The compound has also been prepared by E. von Meyer (*J. pr. Chem.*, 1910, **82**, 521) from resorcinol and triphenylmethyl chloride, the melting point being given as 268°. The true melting point of 2 : 4-dihydroxytetraphenylmethane appears to be considerably higher, for if placed in a bath at 250° and rapidly heated, it does not melt until about 280°.

(6) *Resorcinol dimethyl ether.* 7·50 G. of the condensation product were collected after 15 minutes, and a further quantity (0·5 g.) was obtained by diluting the mother-liquor. The product was extracted with a large volume of boiling acetic acid, and the insoluble material collected. The acetic acid solution deposited crystals, m. p. 180° after recrystallisation from benzene–alcohol. Its properties are in agreement with those of 2 : 4-dimethoxytetraphenylmethane, which was prepared by Gomberg and Forrester (*loc. cit.*) from 2 : 4-dimethoxytriphenylmethyl chloride and magnesium phenyl bromide.

The material insoluble in acetic acid separated from benzene–alcohol in colourless crystals (1·1 g.), m. p. 271° (Found: C, 88·45; H, 6·6. $C_{46}H_{38}O_2$ requires C, 88·7; H, 6·15%). 1 : 3-*Dimethoxy*-4 : 6-*bistriphenylmethylbenzene* is difficultly soluble in most of the common organic solvents but moderately easily soluble in benzene.

(7) *Pyrogallol.* A solution of triphenylcarbinol (6 g.) in acetic acid (50 c.c.) and sulphuric acid (10 g.) was mixed with a solution of pyrogallol (6 g.) in acetic acid (10 c.c.), and after an hour the crystalline product was washed (dilute alcohol) and dried (7·99 g.). Purification of the product was complicated by the presence of another substance (in all probability formed by the di-triphenylmethylation of pyrogallol) whose removal was very difficult, as was shown by the high carbon content of the various preparations. After many recrystallisations from acetone, 3 : 4 : 5-*trihydroxytetraphenylmethane* was obtained as efflorescent colourless prisms which contained two molecules of acetone (Found: loss on heating at 80° in a vacuum, 21·4. $C_{25}H_{20}O_3,2Me_2CO$ requires loss, 24·0%). The pure substance darkens at about 230° and melts with much decomposition at about 255°, the melt being black (Found: C, 81·0; H, 5·5. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5%). 3 : 4 : 5-Trihydroxytetraphenylmethane is difficultly soluble in alcohol, benzene, and acetic acid but easily soluble in hot acetone.

(8) *Pyrogallol trimethyl ether.* At the end of a week the 3 : 4 : 5-*trimethoxytetraphenylmethane* (7·87 g.) was collected, washed (dilute alcohol), dried, and recrystallised from acetic acid; it then formed

colourless needles, m. p. 178° (Found: C, 81·6; H, 6·3. $C_{28}H_{26}O_3$ requires C, 81·9; H, 6·4%).

(9) *α-Naphthol*. 7·25 G. of the reaction product were obtained as in (3). It was boiled with alcohol and the solution, after filtration from an insoluble residue (0·80 g.), deposited colourless clusters of prisms which contained one molecule of alcohol (Found: loss on heating at 80° in a vacuum, 10·5. $C_{29}H_{22}O$,EtOH requires loss, 10·7%). The pure 4-*triphenylmethyl*-1-*naphthol* melted at 204—204·5° (Found: C, 89·9; H, 5·8; *M*, 359. $C_{29}H_{22}O$ requires C, 90·1; H, 5·7%; *M*, 386).

The material insoluble in alcohol was crystallised from acetic acid and recrystallised from aqueous acetone, after which it formed a white powder (Found: C, 91·45; H, 6·1; *M*, 617, 605, 598. $C_{48}H_{36}O$ requires C, 91·7; H, 5·8%; *M*, 628). 2 : 4-*Bistriphenylmethyl*-1-*naphthol* melts at 235—236°.

(10) *β-Naphthol*. The reaction mixture slowly deposited crystals of 1-*triphenylmethyl*-2-*naphthol*, which were collected at the end of a month, washed with dilute alcohol, dried (6·4 g.), and recrystallised from alcohol; m. p. 228° (Found: C, 89·9; H, 5·85. $C_{29}H_{22}O$ requires C, 90·1; H, 5·7%).

(11) *Thymol*. The deep brown reaction mixture was left until the next day; the colour had then faded to light brown. It was poured into water, the mixture boiled, and the resulting oil digested with sodium hydroxide solution, after which it solidified on cooling. It was taken up in ether, and the solution shaken with sodium hydroxide solution and dried over sodium sulphate. After removal of ether, the residue crystallised from methyl alcohol in colourless needles which, after drying in a vacuum over sulphuric acid for 24 hours, melted at 106—107°. At a higher temperature the melt resolidified, and a second and sharp melting occurred at 157°. The low-melting material was heated in a vacuum at 80° (5 hours), then at 110° (4 hours), and finally at 148° (5 hours), a treatment which failed to bring about either an appreciable loss in weight or fusion of the substance. The dried material melted at 157°, and after recrystallisation from methyl alcohol was converted into the lower-melting form. 4-*Hydroxy*-2-*methyl*-5-iso*propyltetraphenylmethane* exists, therefore, in two crystalline modifications melting at 106—107° and 157° (Found in higher-melting form: C, 88·5; H, 7·5. $C_{29}H_{28}O$ requires C, 88·7; H, 7·2%). It is easily soluble in all organic solvents with the exception of cold methyl alcohol.

(12) *o-Chlorophenol*. At the end of 2 months the crude 3-*chloro*-4-*hydroxytetraphenylmethane* was collected, washed (dilute acetic acid), dried (2·1 g.), and recrystallised first from alcohol and then

193·5° (Found : Cl, 9·6. $C_{25}H_{19}OCl$ requires Cl, 9·6%). It is easily soluble in alcohol, benzene, and acetic acid but difficultly soluble in petrol and ether. It is stable towards a boiling mixture of hydriodic and acetic acids (see Part I).

The acetic–sulphuric acid mother-liquor was poured into water and the resulting oil was digested with sodium hydroxide solution, after which it solidified on cooling. The well-washed and dried solid was dissolved in the minimum quantity of benzene, and on addition of alcohol gave colourless crystals of the benzene compound of triphenylmethane, m. p. 78°, which after loss of benzene melted at 93° and weighed 1·66 g. Evaporation of the mother-liquor gave an intractable oil.

(13) m-*Chlorophenol.* The reaction mixture was set aside for a month and was then heated on a boiling water-bath until the deep brown colour had faded. It was then poured into water, and the product worked up as under (12). 1·68 G. of triphenylmethane were isolated.

(14) p-*Chlorophenol.* This experiment was conducted exactly as under (13). 2·4 G. of triphenylmethane (m. p. and mixed m. p. with an authentic specimen, 93°) were isolated, together with an uncrystallisable oil.

(15) o-*Bromophenol.* This experiment was similar to (12) with the exception that the reaction mixture was worked up after one month. The crude *3-bromo-4-hydroxytetraphenylmethane* (1·68 g.) was recrystallised from alcohol, and formed a white crystalline powder, m. p. 186—187° with previous shrinkage (Found : Br, 19·5. $C_{25}H_{19}OBr$ requires Br, 19·3%). From the acetic–sulphuric acid solution triphenylmethane (1·56 g.) was isolated.

(16) p-*Cresol.* *p*-Cresol (3 g.) was added to a cold solution of triphenylcarbinol (3 g.) in acetic acid (30 c.c.) and sulphuric acid (5 g.). The next day the deep brown solution was full of crystals, and at the end of another day the solution was fuchsine-coloured. The crystals (2·43 g.) after recrystallisation from alcohol melted at 93° alone or mixed with triphenylmethane. On working up the acetic–sulphuric acid solution as previously described, a further 0·40 g. of triphenylmethane was obtained. Acidification of the sodium hydroxide extract produced a yellowish-brown precipitate of an amorphous substance (1·45 g.) which was easily soluble in alcohol, acetone, and acetic acid, but difficultly soluble in benzene, petrol, and chloroform. It dissolved in concentrated sulphuric acid to give a fuchsine-coloured solution. The substance shrinks at about 85° and melts between 100° and 110° with evolution of gas.

(17) p-*Tolyl methyl ether.* Sulphuric acid (13 g.) was added to a

solution of triphenylcarbinol (13 g.) and *p*-tolyl methyl ether (6·1 g.; 1 equiv.) in acetic acid (80 c.c.). After a month the mixture was heated on a boiling water-bath for 2 hours, and on cooling deposited almost pure triphenylmethane (10·05 g.). The mother-liquor was worked up as usual and gave a further quantity of triphenylmethane (1·98 g., making in all 12·03 g., *i.e.*, 98·4% of the theoretical yield) together with a fuchsine-coloured resin which was insoluble in sodium hydroxide solution.

(18) p-*Tolyl ethyl ether.* The reaction mixture was warmed at 75° for several hours, and on cooling, triphenylmethane (3·13 g.) separated. A further quantity (1·95 g.) was obtained from the mother-liquor, together with a brown, uncrystallisable oil.

(19) *Quinol dimethyl ether.* This experiment was conducted as described under (13), triphenylmethane (2·76 g.) and an oil being the only products.

(20) *Methyl salicylate.* The orange-red solution was set aside for a month and then poured into water, and the mixture boiled until the precipitated oil had completely changed into a crystalline mass (5·76 g.), m. p. 159°, of almost pure triphenylcarbinol.

The experiments with other members of group III were carried out in like fashion, the recovered triphenylcarbinol being always in almost theoretical yield.

(21) o-*Tolyl ethyl ether.* Crude 4-ethoxy-3-methyltetraphenylmethane (6·06 g.) was isolated as under (3), and after recrystallisation from benzene–alcohol formed colourless prisms, m. p. 144°. The substance is difficultly soluble in alcohol and acetic acid and easily soluble in benzene.

By the condensation of triphenylcarbinol with *o*-toluidine, van Alphen (*Rec. trav. chim.*, 1927, **46**, 501) obtained a base the diazonium sulphate of which furnished a compound (m. p. 143°) when boiled with alcohol. Although no analysis was given, the compound was suggested to be α-2-ethoxyphenyl-βββ-triphenylethane. In view of the revision of the structure of the original base (see Part I) it seemed desirable to re-open the investigation of this derivative.

4-*Amino-3-methyltetraphenylmethane.*—A mixture of triphenylcarbinol (20 g.), *o*-toluidine (16 g.), concentrated hydrochloric acid (10 c.c.), and acetic acid (40 c.c.) was heated under reflux for an hour. The crystalline hydrochloride of the base which separated (26·8 g.) was boiled with a solution of sodium hydroxide (5 g.) in 60% alcohol (150 c.c.) for 2 hours, and the insoluble amine was collected, washed thoroughly with water, and dried (24 g.). After crystallisation from carbon tetrachloride it formed a white powder, m. p. 216—217°. It was diazotised (4 g.) in a mixture of acetic acid (15

c.c.) and sulphuric acid (2 g.) at 30° with amyl nitrite (4 c.c.). After standing for several hours in a warm place (25—28°) the solution was diluted with a considerable volume of ether; the precipitated diazonium sulphate, after being washed with ether and dried in a vacuum, melted at 106—107° with vigorous decomposition.

4-*Ethoxy*-3-*methyltetraphenylmethane*.—The diazonium sulphate (4 g.) was added in small portions to boiling absolute alcohol (60 c.c.) and after partial evaporation of the alcoholic solution, somewhat brownish crystals were deposited (1·4 g.). These, after recrystallisation from acetic acid and then from alcohol, were colourless, m. p. 143° (*Found*: C, 88·4; H, 7·1. $C_{28}H_{26}O$ requires C, 88·8; H, 6·9%). A mixed melting-point determination with the compound prepared from *o*-tolyl ethyl ether and triphenylcarbinol showed no depression.

4-*Chloro*-3-*methyltetraphenylmethane*.—4-Amino-3-methyltetraphenylmethane (15 g.) was diazotised as above, and the diazo-solution poured into boiling cuprous chloride–hydrochloric acid. The mixture was then poured into water, and the precipitated oil extracted with benzene, shaken repeatedly with water, and dried over sodium sulphate. Light petroleum (b. p. 60—80°) was added to the concentrated benzene solution, and the sandy crystals (9·4 g.) which separated were recrystallised repeatedly from acetic acid. 4-*Chloro*-3-*methyltetraphenylmethane* forms somewhat brownish crystals, m. p. 160° (Found: Cl, 8·6, 8·7.* $C_{26}H_{21}Cl$ requires Cl, 9·6%). It is stable towards both sulphuric acid and a mixture of hydriodic and acetic acids.

o-*Diphenylene*-4-*hydroxydiphenylmethane*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CPh\cdot C_6H_4\cdot OH$. —*o*-Diphenylenephenylcarbinol was condensed with phenol as described by Ullmann and Wurstemberger (*Ber.*, 1904, **37**, 73). On boiling the *o*-diphenylene-4-hydroxydiphenylmethane with a mixture of hydriodic and acetic acids it was converted into *o*-diphenylenephenylmethane, m. p. 145° after crystallisation from alcohol.

-*Diphenylyl*-4-*hydroxytriphenylmethane*, $C_6H_5\cdot C_6H_4\cdot CPh_2\cdot C_6H_4\cdot OH$. —Diphenylyldiphenylcarbinol (Schlenk, Herzenstein, and Weickel, *Annalen*, 1910, **372**, 18) (1·5 g.) and phenol (1·5 g.) were dissolved in acetic acid (15 c.c.), and sulphuric acid (2·5 g.) added. The fuchsine-coloured solution was set aside for a week, and the condensation product was then collected, washed (dilute alcohol), dried, and recrystallised three times from acetic acid, *diphenylyl*-4-*hydroxytriphenylmethane* being obtained as white aggregates,

* The low values obtained (by the method of Carius) are probably due to the fact that even after prolonged heating at 320° some substance remained unoxidised.

m. p. 183° (Found: C, 90·15; H, 6·2. $C_{31}H_{24}O$ requires C, 90·25; H, 5·9%).

The same substance was obtained when diphenylyldiphenylmethyl chloride (1 g.) was boiled with phenol (3 g.). The cherry-red solution gave off hydrogen chloride and eventually became almost colourless. The melt was digested with sodium hydroxide solution, and the residue (1·15 g.) crystallised from acetic acid; the product then melted at 183°, alone or when mixed with the previously prepared substance.

Diphenylyl-4-hydroxytriphenylmethane is stable towards a mixture of hydriodic and acetic acids.

The Decomposition of Tetra-arylmethane Derivatives.—Further investigation of the stability of the tetra-arylmethane derivatives has shown that fission of the types mentioned in Part I is fairly general. The following table is a summary of some further results in that connexion (compare Part I, pp. 634, 638).

	Action of sulphuric acid.				Action of *hydriodic–acetic acid.*
	Wt. (g.).	Temp.	*Time* (mins.).	*Yield of* $CPh_3{\cdot}OH$.	
3 : 4-Dihydroxytetraphenylmethane	0·5	50°	30	0·03	Stable.
3 : 4-Dimethoxytetraphenylmethane	0·5	40	20	0·132	Demethylated.
2 : 4-Dihydroxytetraphenylmethane	0·5	40	5	0·144	$CHPh_3$.
2 : 4-Dimethoxytetraphenylmethane	0·5	25	5	0·027	,,
	0·5	25	5	0·022	
3 : 4 : 5-Trihydroxytetraphenylmethane	0·5	40	15	0·083	,,
3 : 4 : 5-Trimethoxytetraphenylmethane	0·5	40	5	0·072	,,
	1·0	22	20	0·146	
4-Hydroxy-2-methyl-5-*iso*-propyltetraphenylmethane	0·5	40	15	0·058	,,
3 : 5-Dibromo-4-hydroxy-tetraphenylmethane		*Stable.*			*Stable.*
1-Triphenylmethyl-2-naphthol	1·0	60	20	Nil.	,,
4-*Triphenylmethyl*-1-naphthol	1·0	18	16 hrs.	0·41	$CHPh_3$.

These decompositions are analogous to those of 2-hydroxytriphenylmethane (Schmidt, *Diss.*, Heidelberg, 1898, p. 26) and of the hexamethyl ether of phloroglucinolphthalein (Lund, J., 1928, 1569). The new data with regard to the decomposition by means of sulphuric acid form additional evidence that the Baeyer–Villiger reaction is reversible.

In conclusion, the author wishes to express his gratitude to Professor D. R. Boyd, D.Sc., for valuable advice and criticism, and to the Chemical Society for a grant which has partly defrayed the cost

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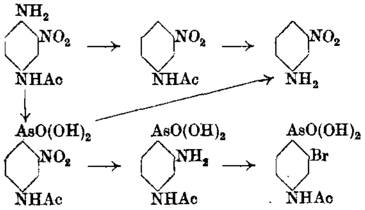
UNIVERSITY COLLEGE,
SOUTHAMPTON. [*Received, February 26th, 1929.*]

CXXX.—*The Chemotherapy of some Bromine Derivatives of Phenylarsinic Acids and Arsenobenzenes.*

By ALAN HAYTHORNTHWAITE.

EHRLICH, in his research on salvarsan, prepared 5 : 5′-di-iodo-3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (Ehrlich and Hata, "Chemotherapy," p. 34), but owing to its chemotherapeutic index being less than that of salvarsan, he did not pursue further the study of halogen derivatives of organic arsenicals.

The present investigation was undertaken to determine the influence on the chemotherapeutic index of the introduction of bromine into the nucleus of some of the simpler phenylarsinic acids and arsenobenzenes. The bromine was introduced in the *o*-, *m*-, and *p*-positions with respect to the arsenic by the use of Sandmeyer's reaction on the corresponding aminophenylarsinic acids. The synthesis and the orientation of the *o*-bromo-acids were carried out as follows :



In no case did the compound produced show an improved chemotherapeutic index when compared with the corresponding compound containing no bromine.

For the determination of the minimum curative dose (C), experiments were performed on mice infected with *Trypanosoma equiperdum* and normal mice were used for the toxicity tests (T). The compounds soluble in sodium hydroxide solution were administered intravenously and those insoluble *per os*.

The following table shows the results obtained.

Compound.	Administration.	*T* (mg. per g.).	*C* (mg. per g.).	*T*/*C*.
Phenylarsinic acid	Intravenous	0·05	>0·05	<1
4-Bromophenylarsinic acid	,,	0·01	>0·01	<1
Arsenobenzene	Per os	0·4	>0·4	<1
4 : 4′-*Dibromoarsenobenzene*	,,	0·05	>0·05	<1
4-Aminophenylarsinic acid	Intravenous	0·2	0·2	1
3-Bromo-4-aminophenylarsinic acid	,,	0·06	>0·06	<1
2-*Bromo*-4-*aminophenylarsinic acid*	,,	0·3	0·3	1
4 : 4′-Diaminoarsenobenzene	Per os	0·1	0·02	5
3 : 3′-*Dibromo*-4 : 4′-*diaminoarsenobenzene*	,,	0·1	0·03	3·3
2 : 2′-*Dibromo*-4 : 4′-*diaminoarsenobenzene*	,,	1·0	0·2	5
4-Acetamidophenylarsinic acid	Intravenous	1·0	0·2	5
2-*Bromo*-4-*acetamidophenylarsinic acid*	,,	2·0	2·0	1
4 : 4′-*Diacetamidoarsenobenzene*	Per os	1·5	0·1	15
2 : 2′-*Dibromo*-4 : 4′-*diacetamidoarsenobenzene*	,,	4·0	0·6	6·7
4-Hydroxyphenylarsinic acid	Intravenous	0·2	0·08	2·5
3-*Bromo*-4-*hydroxyphenylarsinic acid*	,,	0·25	0·25	1
4 : 4′-Dihydroxyarsenobenzene	,,	0·05	0·004	12·5
3 : 3′-*Dibromo*-4 : 4′-*dihydroxyarsenobenzene*	,,	0·02	0·015	1·3
3-Amino-4-hydroxyphenylarsinic acid	,,	2·0	0·3	6·6
5-Bromo-3-amino-4-hydroxyphenylarsinic acid	,,	0·75	0·25	3
3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene	,,	0·125	0·01	12·5
5 : 5′-*Dibromo*-3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene*	,,	0·05	0·025	2
3-Acetamidophenylarsinic acid	,,	1·3	1·0	1·3
5-Bromo-3-acetamido-4-hydroxyphenylarsinic acid	,,	0·3	>0·3	<1
3 : 3′-Diacetamido-4 : 4′-dihydroxyarsenobenzene	,,	0·175	0·03	5·8
5 : 5′-*Dibromo*-3 : 3′-*diacetamido*-4 : 4′-*dihydroxyarsenobenzene*	,,	0·1	0·06	1·7

Since this work was completed a description of 5-bromo-3-amino-4-hydroxyphenylarsinic acid and its acetyl derivative has been given by Fisher and Raiziss (*J. Amer. Chem. Soc.*, 1929, **51**, 527), but the method of preparation is different.

EXPERIMENTAL.

3-Nitro-4-aminoacetanilide was prepared from *p*-aminoacetanilide according to the methods described in the literature (*Ber.*, 1884, **17**, 148), but as these give no definite proof of the position of the nitro-group, its orientation was carried out as follows.

3-Nitro-4-aminoacetanilide (5 g.), suspended in a mixture of 8 c.c. of sulphuric acid (*d* 1·84) and 100 c.c. of water, was diazotised below 10° (sodium nitrite, 1·8 g.; water, 20 c.c.), 100 c.c. of absolute alcohol

were added, and after some time the solid was collected, suspended in 50 c.c. of absolute alcohol, and heated with 2 g. of copper powder until the evolution of nitrogen ceased. The filtered solution, when poured into an excess of water, gave *m*-nitroacetanilide (m. p. 150·5° after recrystallisation from water; yield, 1·9 g.), from which *m*-nitroaniline was obtained on hydrolysis.

2-*Nitro-4-acetamidophenylarsinic Acid* (compare D.R.-P. 267307; Fourneau, Navarro-Martin, and Trefouel, *Ann. Inst. Pasteur*, 1923, 590).—3-Nitro-4-aminoacetanilide (18 g.) was diazotised as described above (concentrated hydrochloric acid, 18 c.c.; water, 30 c.c.; sodium nitrite, 7·2 g.; water, 30 c.c.), the diazo-solution added to copper arsenite solution (Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1921, **43**, 2119) and boiled with charcoal, and the filtered liquid acidified. The arsinic acid obtained (12·8 g.) (Found: As, 24·6. Calc.: As, 24·7%) gave *m*-nitroaniline when boiled with 50% sulphuric acid, and 2-amino-4-acetamidophenylarsinic acid (compare Fourneau, etc., *loc. cit.*) when reduced at 30° by ferrous sulphate (Jacobs, Heidelberger, and Rolf, *J. Amer. Chem. Soc.*, 1918, **40**, 1581) (Found: As, 27·2. Calc.: As, 27·4%).

2-*Bromo-4-acetamidophenylarsinic Acid*.—The preceding amino-acid (30 g.) was diazotised at 0—5° (concentrated sulphuric acid, 36 c.c.; water, 200 c.c.; sodium nitrite, 8 g.; water, 24 c.c.), the solution poured into hot cuprous bromide solution (copper sulphate, 18 g.; copper foil, 14 g.; potassium bromide, 72 g.; water, 90 c.c.) and kept over-night, and the crude acid purified by means of the sodium salt. 2-*Bromo-4-acetamidophenylarsinic acid* (10 g.) separated on acidification (Congo-red) in white irregular plates (Found: As, 21·9; Br, 23·4. $C_8H_9O_4NBrAs$ requires As, 22·2; Br, 23·7%). It crystallised in hexagonal plates from hot water and was soluble in hot alcohol. The barium and calcium salts crystallised in rosettes of needles, the magnesium salt was amorphous.

2-*Bromo-4-aminophenylarsinic Acid*.—30 G. of the preceding acid were refluxed for 10 minutes with 300 c.c. of water and 90 c.c. of concentrated hydrochloric acid. The *amino-acid*, precipitated with sodium acetate solution and purified by Christiansen's method (*J. Amer. Chem. Soc.*, 1920, **42**, 2403), crystallised in white irregular plates (yield, 15 g.) (Found: As, 25·1; Br, 26·6. $C_6H_7O_3NBrAs$ requires As, 25·3; Br, 27·0%). It crystallised from hot water in colourless plates and was soluble in hot alcohol. The calcium and magnesium salts were amorphous.

3-*Bromo-4-hydroxyphenylarsinic acid* was prepared from 3-amino-4-hydroxyphenylarsinic acid (20 g.) in the usual way and purified through the sodium salt (yield, 8·5 g.) (Found: As, 25·4; Br, 26·5. $C_6H_6O_4BrAs$ requires As, 25·3; Br, 26·9%). It was soluble in hot

alcohol and crystallised from hot water in irregular plates. The crystalline calcium salt was insoluble in hot water but very soluble in cold. The magnesium salt was amorphous.

5-Bromo-3-acetamido-4-hydroxyphenylarsinic acid (compare Fisher and Raiziss, *loc. cit.*) (9 g.) was similarly prepared from 5-amino-3-acetamido-4-hydroxyphenylarsinic acid (15 g.) and purified (Found: As, 21·0; Br, 22·4. Calc.: As, 21·2; Br, 22·6%). *It gave* 5-bromo-3-amino-4-hydroxyphenylarsinic *acid in* 60% yield when hydrolysed with 25% sodium hydroxide solution (Found: As, 23·9; Br, 25·4. Calc.: As, 24·0; Br, 25·6%).

The following arsenobenzenes, which are all yellow, amorphous powders, were prepared by means of sodium hydrosulphite from the respective phenylarsinic acids: 4 : 4′-*Dibromoarsenobenzene* (Found: As, 32·2; Br, 32·8. $C_{12}H_8Br_2As_2$ requires As, 32·5; Br, 34·6%); 3 : 3′-*dibromo*-4 : 4′-*diaminoarsenobenzene* (Found: As, 29·3; Br, 29·0. $C_{12}H_{10}N_2Br_2As_2$ requires As, 30·5; Br, 32·5%); 2 : 2′-*dibromo*-4 : 4′-*diaminoarsenobenzene* (Found: As, 28·5; Br, 32·2%); 4 : 4′-*diacetamidoarsenobenzene* (Found: As, 35·0. $C_{16}H_{16}O_2N_2As_2$ requires As, 35·9%); 2 : 2′-*dibromo*-4 : 4′-*diacetamidoarsenobenzene* (Found: As, 25·0; Br, 27·7. $C_{16}H_{14}O_2N_2Br_2As_2$ requires As, 26·0; Br, 27·8%). All the above arsenobenzenes are insoluble in sodium hydroxide solution, and the following are all soluble: 3 : 3′-*Dibromo*-4 : 4′-*dihydroxyarsenobenzene* (Found: As, 29·2; Br, 28·4. $C_{12}H_8O_2Br_2As_2$ requires As, 30·4; Br, 32·4%); 5 : 5′-*dibromo*-3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene* (Found: As, 27·3; Br, 29·1. $C_{12}H_{10}O_2N_2Br_2As_2$ requires As, 28·6; Br, 30·5%): 5 : 5′-*dibromo*-3 : 3′-*diacetamido*-4 : 4′-*dihydroxyarsenobenzene* (Found: As, 25·0; Br, 24·9. $C_{16}H_{14}O_4N_2Br_2As_2$ requires As, 24·7; Br, 26·3%).

THE RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD., WANDSWORTH, S.W. 18. [*Received, March 6th*, 1929.]

CXXXI.—*The Determination of Unsaturated and Aromatic Hydrocarbons in Light Oils and Motor Spirits.*

By ALEXANDER BERNARD MANNING.

IN the course of a systematic examination of the various product of carbonisation of coal at different temperatures and in differen types of retort, the problem arose of determining the compositio of the light oils obtained. The study of these light oils, which hav a boiling range of *ca.* 30—170°, throws considerable light on th

processes occurring during carbonisation, and is of importance also as affecting the utilisation of the refined oils as motor spirits. In analysing light hydrocarbon oils of this character, it is sufficient for most purposes to determine the relative proportions of unsaturated, aromatic, naphthene, and paraffin hydrocarbons. It is evident that, if a method for such a determination is once established, a more complete knowledge of the composition of the oil is readily attained by applying the method to suitably chosen fractions of the origiual oil.

Details of typical methods which have been used for the analysis of light oils will be found in papers by, *e.g.*, Egloff and Morrell (*J. Ind. Eng. Chem.*, 1926, **18**, 354), Kattwinkel (*Brennstoff-Chem.*, 1927, **8**, 353), and Brame (*J. Inst. Pet. Tech.*, 1926, **12**, 48; Brame and Hunter, *ibid.*, 1927, **13**, 794). Sucb methods usually depend on observing the successive losses in volume when the oil is shaken (*a*) with a reagent which absorbs the unsaturated but not the aromatic hydrocarbons, and (*b*) with a secoud reagent which absorbs the aromatic but not tbe saturated hydrocarbons. To avoid the difficulty of completely separating the reagent and the oil, it has been proposed to calculate the percentage of aromatic hydrocarbons in oils from which the unsaturated hydrocarbons have been removed, from the change in some physical property of the oil, *e.g.*, its specific gravity (Thole, *J. Soc. Chem. Ind.*, 1919, **38**, 39T) or its "aniline point" (Tizard and Marshall, *ibid.*, 1921, **40**, 20T), before and after treatment with the reagent. As reagents for the first absorption, sulphuric acids of various concentrations from 80 to 87% have been proposed, but it has been shown (Brame, *loc. cit.*) that the 80% acid will not completely remove the unsaturated hydrocarbons, and the 87% acid attacks the aromatic hydrocarbons. A further difficulty arises from the polymerising action of the acid on the unsaturated hydrocarbons, with the formation of products which are insoluble in the acid. Sulphuric acids of concentrations from 97 to 100%, and also various concentrations of fuming acid, have been proposed as reagents for the removal of aromatic hydrocarbons, but again the difficulty arises of obtaining a sharp separation of the two classes of hydrocarbons. Appreciable errors can arise also from the solubility of the saturated hydrocarbons in the acid solution of the sulphonated aromatic compounds.

Methods of determining the unsaturated hydrocarbons from the bromine or iodine values of an oil can only be regarded as approximate, being liable to relatively large errors (Brame, *loc. cit.*).

Little progress has been made in the problem of determining the relative proportion of cyclic (naphthene) and straight-chain (paraffin) hydrocarbons in the oil from which the unsaturated and aromatic

hydrocarbons have been removed. The use of the "aniline point" for this purpose is hardly legitimate in view of our scanty knowledge of the aniline points of the possible saturated hydrocarbons present in the light oil. Indeed, our limited knowledge of the properties of the individual hydrocarbons which might be present in the light oils under discussion, and the very small number of such hydrocarbons readily available in the pure state for making test mixtures of known composition, constitute fundamental difficulties in any investigation of methods of analysis of complex hydrocarbon oil mixtures.

In the search for a method which would avoid some, at least, of the difficulties discussed above, and which, moreover, could be used when only small quantities of the light oil were available, a line of investigation was followed which was suggested by the methods of gas analysis. A small quantity of the oil, vaporised in a current of air, was passed through a suitable reagent, the increase in weight of which was determined. A convenient and readily available form of apparatus consists of a stoppered U-tube and two potash bulbs in series. The light oil is weighed into the U-tube and the bulbs are charged with the absorbing liquid. A gentle current of dry carbon dioxide-free air (or nitrogen) is passed through the train until the oil has completely vaporised and the absorbing bulbs have attained constant weight. The reagent used is such that the constituent to be absorbed is taken up completely in the first set of bulbs. The function of the second set is discussed later.

With these experimental conditions the complete evaporation of an average sample of light oil (0·2—0·5 g.) requires 2—8 hours, but this could doubtless be expedited by improving the design of the U-tube. To avoid difficulties due to non-volatile residues it is sometimes advisable to redistil the oil immediately before the analysis.

Determination of Aromatic Hydrocarbons in Mixtures containing no Unsaturated Hydrocarbons.—Preliminary experiments on mixtures of this type showed that 98% or even 100% sulphuric acid failed to absorb benzene and toluene completely. The 98% acid, for example took up only about 70% of the benzene present. Complete absorption took place with fuming sulphuric acid (5% SO_3), but this reagent also attacked the saturated hydrocarbons. It was found, however, that the addition of 2—3% of silver sulphate to the 98% acid greatly accelerated the sulphonation of benzene and its homologues, and did not affect the action of the acid on the saturated hydrocarbons. This reagent proved entirely satisfactory for the analysis of these oils. Under the experimental condition

... absorption of the saturated hydro

carbons, varying from 0·1 to 1·0%, but the use of a second set of absorbing bulbs through which only the saturated hydrocarbons pass, permits a correction to be made for this absorption. For instance, in one experiment with a synthetic mixture of benzene and saturated hydrocarbons containing 16·3% of the former, the absorptions in the two sets of bulbs were 17·15 and 0·80% respectively, giving a corrected figure of 16·35% for the aromatic hydrocarbons. The method has been found satisfactory for the determination of aromatic hydrocarbons in motor spirits which do not contain cracked distillates, and for the determination of paraffins in technical benzol, toluol, and xylol. The application of the method is illustrated by the following results :

(I) Synthetic mixture containing 4·4% of benzene and 95·6% of saturated hydrocarbons. Found : 4·45%.

(II) Synthetic mixture containing 48·5% of aromatic hydrocarbons (benzene, toluene, and xylene in approximately equal amounts). Found : 48·4%.

(III) An aviation spirit. Found : 18·4% of aromatic hydrocarbons. Calculated from the weight of aromatic nitro-compounds formed (see below) : 18·5%.

(IV) A technical toluol. Found : 94·3% of aromatic hydrocarbons, *i.e.*, 5·7% of paraffins.

Determination of both Unsaturated and Aromatic Hydrocarbons in Hydrocarbon Mixtures.—Sulphuric acid of various concentrations from 80 to 90% was found incapable of removing unsaturated hydrocarbons completely without attacking aromatic hydrocarbons; moreover some of the unsaturated hydrocarbons polymerised to form volatile compounds which were not retained by the acid. The procedure finally adopted was to absorb unsaturated and aromatic hydrocarbons together in a suitable nitrating mixture (10% concentrated nitric acid, or preferably about 16% of potassium nitrate, in concentrated sulphuric acid), a second absorber being used as before. The correction found is usually somewhat higher (0·5—2·0%) than with the silver sulphate-acid reagent, but the absorption of both unsaturated and aromatic hydrocarbons by the nitrating mixture is complete and difficulties due to polymerisation do not arise. The corrected increase in weight of the absorbing bulbs, therefore, gives the total aromatic and unsaturated hydrocarbon content of the oil. To determine the aromatic hydrocarbons separately they are then isolated in the form of their nitro-derivatives. The solution in the acid mixture, preferably with the addition of a little more nitric acid, is heated in the water-bath for 2—3 hours in order to complete the nitration of the aromatic hydro-

carbons and the oxidation of the unsaturated hydrocarbons. After cooling, the acid solution is poured into excess of water and the nitro-compounds are extracted with three 50 c.c. portions of benzene. The benzene solution is then extracted with a 10% solution of sodium hydroxide, washed with water, evaporated nearly to dryness in a tared flask, dried in a current of air at room temperature, and finally in a vacuum desiccator. The weight of nitro-compounds multiplied by the factor 0·452 gives the weight of the corresponding aromatic hydrocarbons present in the light oil. The value of this factor is based on experiments with the pure hydrocarbons, benzene, toluene, and *m*-xylene, which are converted, respectively, into dinitrobenzene and trinitro-toluene and -*m*-xylene in 96% yield in each case, and the conversion factors calculated on this basis are 0·485, 0·422, and 0·456 respectively; mean 0·452. The other aromatic hydrocarbons which might be present in light oils yield in general trinitro-derivatives, and only in very exceptional oils would they occur in such amount as appreciably to affect this factor. Under the experimental conditions used, the unsaturated hydrocarbons are oxidised almost completely to carbon dioxide, water, and products (presumably acidic) soluble in water or in aqueous sodium hydroxide.

The value for the percentage of aromatic hydrocarbons obtained from the weight of nitro-compounds is, however, always slightly high, owing to contamination with products from the unsaturated hydrocarbons. The error is variable but may be given as roughly one unit on the percentage for every 20% of unsaturated hydrocarbons present. It is serious when the oil contains a high proportion of unsaturated and only small quantities of aromatic hydrocarbons. It can, however, be diminished by removing some of the unsaturated hydrocarbons before passing the vapour into the nitrating mixture. This may be done by interposing in the absorbing train a vessel charged with 70% sulphuric acid, which has no effect on the aromatic hydrocarbons but removes some of the more troublesome of the unsaturated hydrocarbons. It is preferable, therefore, to run two experiments in parallel, one for the determination of the unsaturated and aromatic hydrocarbons together, using the apparatus described, and a second for the separate determination of the aromatics only. A convenient form of train for the latter consists of a U-tube, a set of potash bulbs charged with 70% sulphuric acid, and two stoppered gas-washing bottles of 30—40 c.c. capacity, charged with the nitrating mixture. In this determination it is necessary to weigh only the U-tube. Moreover, the subsequent treatment of the nitrating mixture is facilitated by the use of the gas-washing bottles instead of potash bulbs.

A more accurate value for the percentage of aromatic hydrocarbons and some knowledge of the relative proportions of the different members of the series present are obtained by fractionating the oil through an efficient column, fractions being taken at 95° and 124°. The aromatic hydrocarbons in the three fractions are then determined separately, 0·485, 0·422, and 0·456, respectively, being used as factors for the conversion of the weights of the nitro-compounds into those of the corresponding hydrocarbons. Instead of being weighed, the nitro-compounds may be determined by titration with titanous chloride, but there is no advantage in using this reagent when the total aromatic hydrocarbons are being determined in an oil in which the relative proportions of benzene, toluene, etc., are unknown. The method should always be used, however, for oils high in unsaturated but low in aromatic hydrocarbons, the oil being first fractionated in order to separate the latter. The following results illustrate the use of the method.

	% Calc.	% Found.
I. Synthetic mixture.		
Benzene	39·6	40·2
Amylene	22·1	21·7
Saturated hydrocarbons	38·3	38·1
II. Synthetic mixture.		
Aromatic hydrocarbons (benzene, toluene, and xylene)	7·8	7·8*
Unsaturated hydrocarbons (amylene and hexylene)	12·8	12·3
*cyclo*Hexane, Other saturated hydrocarbons	79·4	79·9

III. Crude light oil from carbonisation of coal at 625°.	Found.	
Benzene	8·2%	24·7% (Benzene, Toluene, Xylene)
Toluene	10·7	
Xylene and higher aromatic hydrocarbons	5·8	
Unsaturated hydrocarbons	42·0	
Saturated hydrocarbons	33·3	
IV. The same light oil after refining.		
Aromatic hydrocarbons	32·5	
Unsaturated hydrocarbons	28·5	
Saturated hydrocarbons	39·0	
V. A power petrol.		
Aromatic hydrocarbons	8·9	
Unsaturated hydrocarbons	16·8	
Saturated hydrocarbons	74·3	
VI. A light oil obtained from the hydrogenation ("berginisation") of coal.		
Benzene	3·4%	27·6% (Benzene, Toluene, Xylene)
Toluene	6·2	
Xylene and higher aromatic hydrocarbons	18·0	
Unsaturated hydrocarbons	10·4	
Saturated hydrocarbons	62·0	

* By titration; but 8·5% from the weight of nitro-compounds.

A few points of interest which have arisen during the present investigation may be mentioned.

When amylene is vaporised in a current of air and passed into 97% sulphuric acid, it is at first apparently absorbed, but soon begins to separate again on the surface of the acid as an insoluble mixture of polymerides, which are slowly volatilised with continued passage of air until almost the whole of the amylene is again removed from the acid. This result confirms the observation of Ormandy and Craven (*J. Soc. Chem. Ind.*, 1928, **47**, 317T) on the polymerisation of olefins by sulphuric acid. No such polymerisation occurs when amylene is passed into the nitrating mixture or into sulphuric acid containing 10% of chlorosulphonic acid.

Under the experimental conditions above described, aromatic hydrocarbons are attacked to a greater or less extent by sulphuric acid of 80% or higher concentration, but not by 70% acid.

When benzene is passed into the nitrating mixture the product of the reaction even in the cold is dinitrobenzene; no mononitrobenzene is formed. The dinitrobenzene remains unchanged during the subsequent heating. Toluene is converted directly into the dinitro-derivative in the cold, but on heating to 100° this is further nitrated to trinitrotoluene.

An attempt is being made to extend the method in order to obtain some information as to the composition of the saturated hydrocarbons.

In conclusion, the author wishes to express his thanks to the Director of Fuel Research for permission to publish the present communication.

H.M. Fuel Research Station,
East Greenwich, S.E. 10. [*Received, January 31st*, 1929.]

CXXXII.—*Some Derivatives of Arylthioarsinous Acids.*

By Harry James Barber.

The formation of metallic derivatives of almost all aliphatic and aromatic thiol compounds is well known; of particular interest are those derived from a thiol compound containing an acidic group capable of forming neutral salts, *e.g.*, α-thiolacetic acid. The metallic thiolacetates constitute a means of obtaining metals in neutral aqueous solution in a non-ionised condition and may therefore find therapeutic application. The great therapeutic activity of aromatic arsenicals containing tervalent arsenic as compared with the corresponding arsinic acids renders the preparation of solubl

derivatives of these important and it seemed likely that thiolacetates and other compounds of that type could be obtained from arylarsenious oxides and dihalogenoarsines in the same way as from arsenious oxide. This was found to be the case, the normal reaction to be expected taking place with formation of an arylthioarsinite :

$$\mathrm{Ar{\cdot}As{:}O + 2RSH \longrightarrow Ar{\cdot}As(SR)_2 + H_2O.}$$

The part of the present work dealing with the above reaction has been anticipated in some degree by Kharasch in an American patent (No. 1,677,392).

A study of the properties and reactions of the di(carboxymethyl) arylthioarsinites led to the discovery that in acid, alkaline, or neutral solution the thiol group of an organic thiol compound reduces the quinquevalent arsenic atom of an arsinic acid to the tervalent state, and the compound produced combines with the excess of the thiol compound, giving the same compound as would be produced from the tervalent arsenic derivative according to the above equation. The reaction is represented thus :

$$\mathrm{Ar{\cdot}AsO(OH)_2 + 4RSH \longrightarrow Ar{\cdot}As(SR)_2 + 3H_2O + RS{\cdot}SR.}$$

This method serves for the preparation of all the compounds of the above type for which it has been tested up to the present and is of much wider application than that involving the tervalent arsenic derivative, since it is frequently a matter of some difficulty to prepare the arylarsenious oxide or dihalogenoarsine by the usual methods from the arsinic acid.

The di(carboxymethyl) arylthioarsinites are in general well-defined crystalline solids. Acid does not liberate thiolacetic acid; nor does hydrolytic fission occur with alkali, as the alkali-metal salts of the di(carboxymethyl) arylthioarsinites can be obtained from strongly alkaline solutions. These salts are neutral and generally extremely soluble in water and have pronounced therapeutic activity. In alkaline solution the arylthioarsinites give an intense nitroprusside reaction, although it has been shown that no fission to free thiol compound has occurred. They can be titrated with iodine in acid or in bicarbonate solution,

$$\mathrm{Ar{\cdot}As(SR)_2 + 2I_2 + 3H_2O \longrightarrow Ar{\cdot}AsO(OH)_2 + 4HI + RS{\cdot}SR;}$$

the same end-point is obtained with nitroprusside as an external indicator as with starch. This shows that the oxidation does not involve oxidation of the thiol or potential thiol groups, followed by the oxidation of the tervalent arsenic atom to the quinquevalent state. The arylthioarsinites are oxidised in alkaline solution by atmospheric oxygen to the parent arsinic acids, this process being much more rapid than is the case with the corresponding aryl-

arsenious oxides. Moreover the oxidation of the latter is accelerated by the presence of the disulphide form of the thiol compound.

This oxidation is being studied in detail, as it is obviously a type of reaction which may occur in the body on administration of such thiol compounds. The biological significance of this reaction and the reduction of arsinic acids by thiol groups will probably be discussed elsewhere. The arylthioarsinites are reduced by sodium hyposulphite to the corresponding arseno-compounds in the same way as are arsinic acids and arylarsenious oxides.

The molecular-weight figures are those found by means of iodine titration according to the equation given above.

EXPERIMENTAL.

Di(carboxymethyl) 4-Aminophenylthioarsinite, $NH_2{\cdot}C_6H_4{\cdot}As(S{\cdot}CH_2{\cdot}CO_2H)_2$.—4-Aminophenylarsinic acid (2·2 g.) is added to a neutral solution of thiolacetic acid (3·8 g.) in 40 c.c. of *N*-sodium hydroxide. The arsinic acid dissolves and the solution remains neutral. On acidification with acetic acid the *thioarsinite* crystallises. It is sparingly soluble in cold water, more readily in hot, readily soluble in glacial acetic acid, and crystallises from hot water or dilute acetic acid in needles, m. p. 142—143° (Found: As, 22·1; N, 4·2; *M*, by iodine titration, 356. $C_{10}H_{12}O_4NS_2As$ requires As, 21·5; N, 4·0%; *M*, 349).

Di(carbethoxymethyl) 4-Aminophenylthioarsinite.—A solution of 4-aminophenylarsinic acid (2·2 g.) in 2*N*-hydrochloric acid (20 c.c.) is stirred with ethyl thiolacetate (5 g.) and after an hour the *hydrochloride* of the required ester is collected, washed free from ethyl dithiodiacetate with ether, and recrystallised by solution in water and addition of excess of hydrochloric acid. It forms needles, m. p. 100—105°, soluble in but hydrolysed by water; it is also soluble in alcohol and acetic acid but insoluble in ether (Found: As, 16·7. $C_{14}H_{20}O_4NS_2As,HCl$ requires As, 17·0%). The free base has only been obtained as an oil insoluble in water but readily soluble in organic solvents. In cold alkali the carbethoxy-group is hydrolysed, the di(carboxymethyl) thioarsinite being formed.

Di(carbamylmethyl) 4-aminophenylthioarsinite may be obtained from the preceding ester and aqueous ammonia but is most readily prepared by adding 4-aminophenylarsinic acid (2·2 g.) to a hot solution of thiolacetamide (3·8 g.) in 50 c.c. of water; on cooling, it separates in colourless needles, m. p. 145°, sparingly soluble in cold water, readily soluble in hot water and glacial acetic acid (Found: As, 21·6; N, 11·9; *M*, by iodine titration, 347. $C_{10}H_{14}O_2N_3S_2As$ requires As, 21·6; N, 12·1%; *M*, 347).

Di(carboxymethyl) 3-Amino-4-hydroxyphenylthioarsinite.—This is prepared from 3-amino-4-hydroxyphenylarsinic acid (2·3 g.) by the method used for the 4-amino-compound. It is dissolved in the minimum quantity of 25% sodium hydroxide solution required to give a solution neutral to litmus, and excess of alcohol added; the disodium salt then crystallises in needles. The pure *acid* recovered from this crystallises in colourless prismatic needles, m. p. 157—158°, sparingly soluble in cold water and alcohol, more readily soluble in hot, and readily soluble in glacial acetic acid (Found: As, 20·2; N, 3·8; S, 17·6; *M*, by iodine titration, 363. $C_{10}H_{12}O_5NS_2As$ requires As, 20·5; N, 3·8; S, 17·5%; *M*, 365).

Di(carbamylmethyl) 3-amino-4-hydroxyphenylthioarsinite forms needles, m. p. 132—133° (Found: As, 21·1; N, 11·5; *M*, 363. $C_{10}H_{14}O_3N_3S_2As$ requires As, 20·65; N, 11·6%; *M*, 363).

Di(β-carboxy-β-aminoethyl) 3-Amino-4-hydroxyphenylthioarsinite.—A warm solution of 3-amino-4-hydroxyphenylarsinic acid (2·3 g.) and cysteine hydrochloride (6·5 g.) in 100 c.c. of water is neutralised with ammonia, and the product filtered off rapidly before the cystine produced crystallises. The product, after solution in dilute hydrochloric acid (charcoal) and recovery, crystallises in very fine, matted needles (Found: As, 17·5; N, 9·9. $C_{12}H_{18}O_5N_3S_2As$ requires As, 17·7; N, 9·9%).

Di(carboxymethyl) 5-Acetamido-2-hydroxyphenylthioarsinite.—5-Acetamido-2-hydroxyphenylarsinic acid (5·5 g.) is added to a solution of thiolacetic acid (7·5 g.) in benzene (50 c.c.) and stirred well for a few minutes. The arsinic acid changes to a clear oil which then rapidly crystallises. The *product* is filtered off, washed with ethyl acetate (to remove dithiodiacetic acid), and recrystallised from hot water; m. p. 172—174° (Found: As, 18·6; *M*, 403. $C_{12}H_{10}O_4N_3S_2As$ requires As, 18·5%; *M*, 405).

Di(carboxymethyl) 4-Carbamylmethylaminophenylthioarsinite.—Sodium *N*-phenylglycineamide-4-arsinate ("tryparsamide") (6·1 g.) is dissolved in water (50 c.c.), and thiolacetic acid (7·2 g.) in 2*N*-sodium hydroxide (40 c.c.) added. On acidification with hydrochloric acid the *product* is obtained as an oil which crystallises. It is purified through its sodium salt (square plates) and obtained from hot water in long slender prisms, m. p. 90° (Found: As, 18·1; *M*, 407. $C_{12}H_{15}O_5N_2S_2As$ requires As, 18·5%; *M*, 406).

Di(carboxymethyl) 8-acetamido-3-hydroxy-1 : 4-benzisooxazine-6-thioarsinite is obtained from the corresponding arsinic acid (Newbery, Phillips, and Stickings, J., 1928, 3060) in a similar way, and crystallises in needles, m. p. 212° (decomp.) (Found: As, 16·1; *M*, 460. $C_{14}H_{15}O_7N_2S_2As$ requires As, 16·2%; *M*, 462).

Di(carbamylmethyl) 8-acetamido-3-hydroxy-1 : 4-benzisooxazine-

6-thioarsinite, obtained in the usual way from the arsinic acid and thiolacetamide in aqueous solution, forms needles, m. p. 233—235°, from 25% acetic acid (Found: As, 16·9; *M*, 464. $C_{14}H_{17}O_5N_4S_2As$ requires As, 16·3%; *M*, 460).

Di(β-*carboxy*-β-*aminoethyl*) 8-*acetamido*-3-*hydroxy*-1 : 4-*benziso-oxazine-6-thioarsinite*, obtained from the arsinic acid and cysteine hydrochloride in the manner described above for the 3-amino-4-hydroxyphenylarsinic acid, crystallises in extremely fine, matted needles which set to a gel-like substance (Found: As, 13·8. $C_{16}H_{21}O_7N_4S_2As$ requires As, 14·4%).

Di(β-*hydroxyethyl*) 8-*acetamido*-3-*hydroxy*-1 : 4-*benzisooxazine* 6-*thioarsinite*, obtained from the arsinic acid (3·3 g.), dissolved in a slight excess of dilute aqueous ammonia, and β-hydroxyethyl mercaptan (3·2 g.), crystallises in needles (Found: As, 17·8. $C_{14}H_{19}O_5N_2S_2As$ requires As, 17·3%).

RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD.,
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CXXXIII.—*Thiolacetamide as a Reagent for identifying Arsinic Acids.*

By HARRY JAMES BARBER.

A DIFFICULTY frequently encountered in the chemistry of organic arsenic derivatives is that of establishing the identity of a product. It is the exception rather than the rule for an arsinic acid to have a true melting point. The comparison of the calcium, barium, and magnesium salts under standard conditions (King and Murch, J., 1924, **125**, 2601) is a useful but by no means decisive guide.

Arsinic acids are reduced by thiol compounds (see preceding paper) and it is shown here that the di(carbamylmethyl) arylthio-arsinites which can be prepared by that method have, in general, definite melting points which are depressed by admixture with other di(carbamylmethyl) arylthioarsinites. It is suggested that these well-defined crystalline compounds may be a valuable additional means of identifying and characterising arsinic acids. The preparation is very simple and can be carried out with small amounts of material; moreover, the arsinic acid can be recovered by mild oxidation of the thioarsinite. The conditions for the preparation are varied somewhat according to the nature of the arsinic acid. In the normal case the arsinic acid is added to a hot aqueous solution of thiolacetamide (4 mols.); the arsinic acid dissolves, and the

thioarsinite crystallises on cooling. The reaction is represented by the equation $Ar{\cdot}AsO(OH)_2 + 4SH{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \longrightarrow$

$$Ar{\cdot}As(S{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2 + ({\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2 + 3H_2O.$$

With sparingly soluble arsinic acids it is more convenient to use a solution of the sodium salt of the arsinic acid, and with nitro-compounds the reaction should be carried out in the cold to minimise the possibility of reduction of the nitro-group by the thiol compound. The thioarsinites can be recrystallised from hot water or from aqueous acetic acid and can be estimated rapidly by direct titration with standard iodine solution.

$$Ar{\cdot}As(S{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2 + 2I_2 + 3H_2O \longrightarrow Ar{\cdot}AsO(OH)_2 + ({\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2 + 4HI.$$

EXPERIMENTAL.

The following table, which gives the data for a number of typical arsinic acids, serves as an indication of the use of the method. The melting points are uncorrected figures. In the case of the higher-melting substances it is more satisfactory to heat the melting-point bath fairly rapidly so as to obtain sharper melting points. The molecular weights recorded were determined by dissolving 0·2 g. of thioarsinite in 50 c.c. of warm 2*N*-acetic acid, adding 50 c.c. of water, and titrating the warm solution (usually at about 40°) with *N*/10-iodine, with starch as indicator.

		Thioarsinite.		Molecular wt.	
	Arsinic acid.	M. p.	Formula.	Calc.	Found.
a	Phenyl	129—130°	$C_{10}H_{13}O_2N_2S_2As$	332	331
b	2-Aminophenyl	140	$C_{10}H_{14}O_2N_3S_2As$	347	351
c	4-Aminophenyl	145	$C_{10}H_{14}O_2N_3S_2As$	347	347
d	2-Hydroxyphenyl	161—163	$C_{10}H_{13}O_3N_2S_2As$	348	348
e	4-Hydroxyphenyl	160—162	$C_{10}H_{13}O_3N_2S_2As$	348	351
f	3-Amino-4-hydroxyphenyl	132—133	$C_{10}H_{14}O_3N_3S_2As$	363	363
g	3-Acetamido-4-hydroxyphenyl	176	$C_{12}H_{16}O_4N_3S_2As$	405	405
h	5-Acetamido-2-hydroxyphenyl	188	$C_{12}H_{16}O_4N_3S_2As$	405	408
i	3-Amino-4-methylaminophenyl	141—143	$C_{11}H_{17}O_2N_4S_2As$	382	376
j	4-Chlorophenyl	134—136	$C_{10}H_{12}O_2N_2ClS_2As$	366·5	371
k	4-Chloro-3-nitrophenyl	142—143	$C_{10}H_{11}O_4N_3ClS_2As$	411·5	418
l	3 : 5-Diamino-4-hydroxyphenyl	159—161	$C_{10}H_{15}O_3N_4S_2As$	378	381
m	2 : 6-Diacetamidophenoxyacetic acid 4-arsinic acid	157	$C_{16}H_{21}O_7N_4S_2As$	520	532
n	8-Acetamido-3-hydroxy-1 : 4-benzisooxazine-6-arsinic acid	233—235	$C_{14}H_{17}O_5N_4S_2As$	460	464

Mixtures of the preceding di(carbamylmethyl) arylthioarsinites

melt as follows: *b* and *c*, 124°; *d* and *e*, 142°; *a* and *f*, 110—115°; *g* and *h*, 150°; *c* and *f*, 125°.

My best thanks are due to Dr. Ewins for the interest he has shown in the work of this and the preceding paper.

RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD.,
WANDSWORTH, S.W. 18. [*Received, March 7th*, 1929.]

CXXXIV.—*The Dielectric Constant of Desiccated Oxygen.*

By HARRY LISTER RILEY.

IT has been shown that the prolonged drying of oxygen leads to a pronounced decrease in its chemical activity. Dry oxygen does not combine with dry carbon, sulphur, phosphorus, hydrogen, carbon monoxide, etc., at temperatures at which normally combination takes place readily. This change in chemical activity is accompanied by an alteration in the dielectric strength of a gas: Thomson (*Phil. Mag.*, 1893, **36**, 313) has shown that the potential necessary to cause an electric spark to pass through a gas which has been dried by phosphoric oxide is considerably greater than that required in an ordinary gas.

This investigation was undertaken in order to determine whether or no this change in chemical and electrical properties is accompanied by some fundamental change in the structure of a gaseous molecule, of such a nature as to alter the specific inductive capacity. The thermionic valve enables the electrical capacity of a condenser to be measured with extreme accuracy, and it was therefore decided to compare the capacities of two condensers, one containing ordinary dry oxygen, and the other, oxygen that had been subjected to the action of phosphoric oxide over a prolonged period.

Two similar electrical condensers, consisting of cylindrical silver plates (0·5 mm. thick), enclosed in glass tubes, were constructed. The plates were held rigidly apart at each end by means of four tapering glass plugs, which fitted tightly in holes bored through the inner cylinder (see Figs. 1 and 2). Before the cylinders were introduced into the glass tubes, the latter were thoroughly cleaned and heated to dull redness in a current of dry air. After being etched with dilute nitric acid, washed with water, and dried, the silver cylinders were introduced into the glass tubes, and the platinum leads sealed through the glass. The condenser which was to contain desiccated oxygen as dielectric was then placed in an air-bath and heated at 350° for 48 hours while it was alternately evacuated and

filled with pure dry oxygen. The oxygen, which was prepared by the electrolysis of specially purified baryta, was passed over heated copper oxide, to remove hydrogen, and dried by passing through tubes containing caustic potash and redistilled phosphoric oxide. After this treatment, the side-tube A of the condenser was opened, and some pure, redistilled phosphoric oxide introduced, the tube being quickly resealed. The condenser was again evacuated, filled with pure dry oxygen, and the process repeated six times, the vessel being finally closed by sealing. The other condenser was filled in a

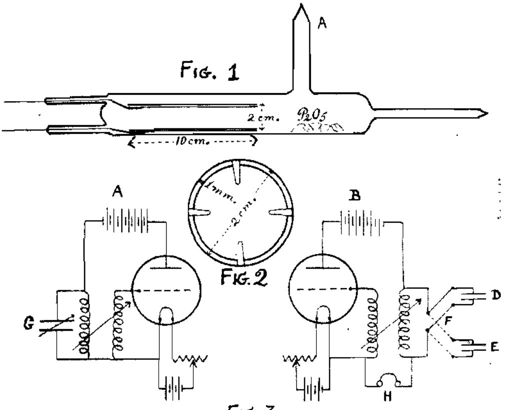


Fig. 1

Fig. 2

Fig. 3

similar manner, but no phosphoric oxide was introduced, and the oxygen was dried by passing over calcium chloride.

The method employed in comparing the capacities of the two condensers was essentially that described by Whiddington (*Phil. Mag.*, 1920, **40**, 634). The apparatus, shown in diagram in Fig. 3, consists of two oscillating valve circuits, A and B; D and E are the two condensers and either can be placed in the circuit B by means of the switch F. In carrying out a comparison, one of the condensers is placed in circuit and the variable condenser G tuned until a suitable note is produced in the telephones H. By turning the switch F, the other condenser can be brought into circuit and the note produced compared with the original one. The two condensers used were of the same dimensions (capacity 0·00005 micro-

farad), and gave notes of almost identical pitch. The capacities of the two condensers have been compared at intervals during 10 months, and not the slightest change in capacity of the condenser containing phosphoric oxide has been detected. Considering the accuracy of the method, this result appears to indicate that the action of very small traces of water vapour in promoting chemical activity is not to be explained by any change in the structure of the molecule on drying.

The author is indebted to Professor H. B. Baker for advice and suggestions during this investigation, and to the Royal Society, a grant from whom partly covered the cost of the apparatus.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, March 13th*, 1929.]

CXXXV.—*An Enquiry into the Cause of Periodic Phenomena in Electrolysis.*

By ERNEST SYDNEY HEDGES.

A CONSIDERABLE amount of data concerning periodic processes in electrolysis has been accumulated in recent years (Hedges, J., 1926, 1533, 2580, 2878; 1927, 1077; 1928, 969), and the systems studied have included periodic phenomena both at the anode and at the cathode. Whilst in every case the conditions of periodicity have been defined and it has been possible to deduce a number of generalities from the results, and even to forecast whether a given system is likely to exhibit periodicity, the experiments described so far have not been able to discriminate between the various explanations of the cause of the periodicity.

In an endeavour to elucidate the mechanism, some experiments with rotating anodes are now described and may be regarded as complementary to the series mentioned above.

EXPERIMENTAL.

The system chosen for investigation was the anodic dissolution of copper in hydrochloric acid, since this gives an effect of the greatest magnitude.

Apparatus.—The apparatus and conditions of experimentation were as described in the former papers (*locc. cit.*), except for the arrangement of the anode. The device adopted for rotating the anode was as follows. A nickel rod, provided with a nickel screw and washer for affixing the metal to be used as anode, is fitted tightly into a small wooden pulley by means of an indiarubber slip. The

upper side of the pulley is bored, so as to hold a pool of mercury, which covers the end of the nickel rod. The mercury pool is partly covered by a thin card, leaving a small aperture for insertion of a lead connecting the electrode with the source of current and the string electrometer. The object of the card is to retain the mercury, which is otherwise centrifuged when high speeds are used. The electrodes were made of electrolytic sheet copper, measuring $6 \times 1 \times 0{\cdot}1$ cm., and a length of 3 cm. of the electrode was immersed in the hydrochloric acid.

The Relation between Frequency and Current Density.—When a copper anode dissolves in not too dilute hydrochloric acid at low *C.D.*'s, cuprous chloride is formed and dissolves in the acid, but at high *C.D.*'s an oxidic film covers the anode and the current passing falls to a very low value. At intermediate *C.D.*'s, the two states alternate, the copper becoming covered with a dark film periodically, whilst periodic changes in *C.D.* and *P.D.* take place simultaneously (J., 1926, 1533). In the former experiments, the solution was kept in circulation by means of a stream of air or hydrogen bubbles, and it was found that the rate of stirring did not affect the results unless the stream was allowed to travel directly up the anode. Evidently, such a method of circulation is quite ineffective in regard to the solution in the immediate vicinity of the electrode surface, for the use of a rotating anode brings out quite different relations.

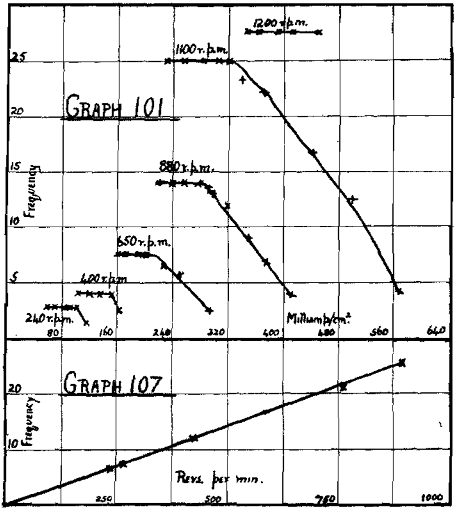
With a stationary anode, the frequency of the periods decreased rapidly with increasing *C.D.* On the other hand, with a rotating anode, the frequency is independent of *C.D.* over a certain range and later decreases almost linearly with increasing *C.D.* This is shown by Graph 101 (Fig. 1), in which the frequency (number of waves per sec. $\times$ 100) has been plotted against the *C.D.* The system represented is a copper anode in 25% hydrochloric acid (% by vol. of acid of *d* 1·16) and each curve refers to a different speed of rotation, varying between 240 and 1200 r.p.m. The graph shows (1) that the critical *C.D.* for periodicity increases with speed of rotation, (2) that there is a "characteristic frequency," independent of *C.D.* and increasing with speed of rotation, and (3) that a second critical *C.D.* exists, at which the frequency ceases to be independent of *C.D.* and which also rises with speed of rotation. The measurements of frequency were taken by altering the *C.D.* and observing the time for 10 successive waves by means of a stop-watch. The measurements in Graph 101 are not regarded as having the same degree of accuracy as those in the following graphs, since improvements were subsequently made in the control of the speed of rotation.

The existence of a characteristic frequency, independent of *C.D.* and increasing with the speed of rotation, indicates at once that the

frequency is not dependent on the rate at which metal ions leave the electrode. That the phenomenon is quite independent of the velocity of dissolution of a metal is confirmed by previous work on the periodic formation of films at an unattackable anode (J., 1926, 2591).

The most probable interpretation of the second part of each curve, where frequency decreases with increasing *C.D.*, is that at a sufficiently high *C.D.* some product begins to accumulate on the anode.

Fig. 1.



Until this second critical *C.D.* is reached, the rotation is rapi enough to wash away the product as fast as it is formed. The ris of the second critical *C.D.* with increasing speed of rotation is coı sistent with this view. It will be shown later that the produ concerned is cuprous chloride.

The Relation between Frequency and Speed of Rotation at Consta Concentration.—Graph 107 (Fig. 1) shows the relation betwee frequency and speed of rotation for a copper anode in 40% hydr

chloric acid. The readings on this graph were made by determining the frequency–*C.D.* curve for each speed and then plotting the "characteristic frequency" (see above) against the speed. The points lie on a straight line passing through the origin. It appears, therefore, that the frequency is independent of the rate of dissolution of the anode, but is in direct proportion to the speed of rotation. The graph indicates that one complete period is produced for every 58 revolutions (approx.) of the electrode, independently of the rate of revolution. (*Note.* In this graph frequencies are in seconds and revolutions in minutes.)

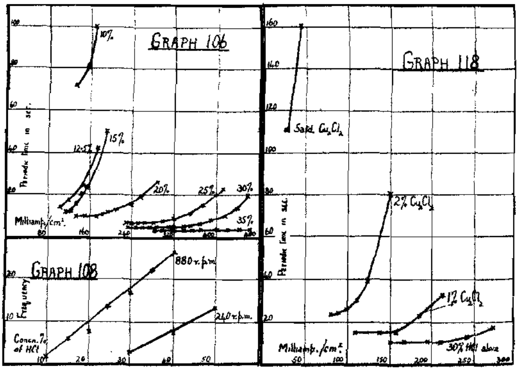
Variation of the speed of rotation can produce two effects: (1) the anodic product is washed away more rapidly, (2) chlorine ions are supplied to the anode at a greater rate. If the frequency were determined by the first of these effects, it would not be independent of *C.D.*; consequently, it may be inferred that the frequency is controlled by the rate of supply of chlorine ions to the anode.

The Relation between Frequency and Current Density at Constant Speed for Different Concentrations.—Apart from variation in the speed of rotation, the rate of supply of chlorine ions to the anode can be varied by altering the concentration of the hydrochloric acid. Experiments have been carried out with solutions of hydrochloric acid varying in concentration between 10 and 40%, a constant speed of 880 r.p.m. being used, and the results are shown in Graph 106 (Fig. 2). Instead of plotting the frequency, its reciprocal—the "periodic time" or duration of a period in seconds—has been plotted against the *C.D.* As expected from the considerations given above, both the critical *C.D.* required to produce the periods and the characteristic frequency increase with the concentration of acid. The graph also shows that the independence between frequency (or periodic time) and *C.D.* is not realised in solutions of hydrochloric acid whose concentrations are below 20% and that the region of independence is more marked the higher the concentration. This suggests that the product responsible for the change of frequency with *C.D.* at low speeds and low concentrations is cuprous chloride, which is far more readily soluhle in the concentrated acid. Some experiments have therefore been conducted in which 1%, 2%, or an excess of cuprous chloride was added directly to a system consisting of a copper anode rotating at 880 r.p.m. in 30% hydrochloric acid, and the results are represented by Graph 118 (Fig. 3). With increasing amounts of cuprous chloride, both the critical *C.D.* required to produce periods and the frequency of the periods are lowered, and the horizontal part of the curve, indicating independence between frequency and *C.D.*, is destroyed. In fact,

Graph 118 is precisely similar to Graph 106, and it may therefore be inferred that cuprous chloride is the responsible product.

The amplitude of the periods obtained with a rotating anode is, *in general, less than that of the periods with a stationary anode.* The amplitude is about 1 volt during the stage where frequency is independent of *C.D.*, but increases considerably after the second critical *C.D.* has been passed. With a stationary anode, amplitudes of about 12 volts were recorded. This suggests that when cuprous chloride begins to collect at the anode, a much thicker oxide film is produced—probably by hydrolysis of the cuprous chloride.

FIG. 2. FIG. 3.



The Relation between Frequency and Concentration at Constant Speed.—If the frequency is determined by the rate of supply of chlorine ions to the anode, a linear relation between frequency and concentration of hydrochloric acid is to be expected. That this is realised is shown by Graph 108 (Fig. 2), where the characteristic frequency is plotted against concentration for two different speeds, *viz.*, 880 and 240 r.p.m. The points were obtained by determining the frequency–*C.D.* curve for each concentration, and plotting the value of the frequency corresponding to the horizontal portion of the curve.

Discussion.

The experiments indicate that the frequency of the periods is independent of the *C.D.*, but proportional to the rate of stirring and

to the concentration of the acid. Three factors can be concerned in determining the frequency : (1) rate of removal of ions from the metal, (2) rate of removal of anodic product, (3) rate of supply of chlorine ions to the anode. Since (1) and (2) are dependent on the *C.D.*, it may be inferred that the rate of diffusion of chlorine ions is the controlling factor. The distinction between (1) and (3) holds only at these high *C.D.*'s considered—*i.e.*, above the critical *C.D.* At low *C.D.*'s it is not possible to distinguish between (1) and (3), but at high *C.D.*'s negative ions other than chloride (*e.g.*, hydroxyl) compete; the rate of supply of chlorine ions is determined by the *stirring, and the rate of ionisation of the metal is determined* by the *C.D.*

The following view of the mechanism is taken. At low *C.D.*'s cuprous chloride is formed at the anode : this, being soluble in the acid solution, is washed away from the anode continuously, and fresh chlorine ions diffuse in continuously. The *P.D.* therefore remains constant at a low value. It is to be noted that in the formation of the cuprous chloride–hydrochloric acid complex the chlorine ions are removed, as such, from the sphere of action. At a certain critical *C.D.*, the rate of disposal of chlorine ions begins to overtake the rate of diffusion of fresh chlorine ions to the electrode. This produces two effects : (*a*) the scarcity of chlorine ions in the layer of liquid immediately contiguous to the anode allows hydroxyl ions to be discharged, and (*b*) hydrogen ions migrate away from the positively charged anode. The effect (*b*) tends to make the layer of liquid alkaline. The discharge of hydroxyl ions (*a*) makes the anolyte as a whole more acid, but the hydrogen ions so produced migrate from the vicinity of the electrode according to (*b*). It is necessary to distinguish between this thin alkaline liquid sheath and the anolyte as a whole, which, of course, tends to become more acid. The thin alkaline sheath is of greater importance in the behaviour of the anode. Both effects (*a*) and (*b*) have the same result—the formation of an oxidic film (basic salt or oxide) on the metal, (*a*) by direct discharge of hydroxyl ions, or (*b*) by hydrolysis of the primary anodic product. This film, which is visible, explains the rise in potential, or passivity in its widest sense.

In the case of the easily passivated metals, such as iron, the visible film reduces the active area of the electrode, raising enormously the effective *C.D.* at the uncovered spots, so that an invisible, highly protective oxide film forms at these points and rapidly spreads to cover the entire electrode according to the mechanism suggested in a previous paper (J., 1928, 977).

The subsequent fall of potential is due to the action of the hydrochloric acid on the oxidic film, changing it to cuprous chloride, which

subsequently dissolves in the acid. This change is easily visible and its direction of propagation over the electrode always follows the direction of flow of the hydrochloric acid, which can be varied at will. It is easy to see that after the fall of potential, the original *C.D.* being reinstated, the oxidic film will form again. The fundamental problem is why the dissolution of the film takes place in definite periods instead of there being set up a state of dynamic equilibrium. The experiments showing that the frequency depends entirely on the rate of accumulation of chlorine ions appear to leave no escape from the conclusion that dissolution of the film does not occur until a certain critical concentration is reached, but that when reaction occurs in each "pulse" it is complete. This is analogous to the "all-or-nothing" law so familiar in physiology, according to which a system does not respond to a stimulus until this reaches a threshold value, but the response is complete when that value is reached. Evidence of the existence of such critical concentrations will be given later.

A view frequently expressed with regard to the older cases of periodic electrolysis is that the resistance of the film decreases the current, so allowing the ions to collect by diffusion until they attack the film, and the consequent increase in current brings about once more the condition for the formation of a new film. As Ostwald pointed out long ago (*Z. physikal. Chem.*, 1900, **35**, 210), two such continuous processes would not produce a periodic course, but would set up a dynamic equilibrium condition, where the rates of formation and dissolution of the film substance were equal. In order to account for periodicity, a *discontinuity* must occur somewhere in the process. It is interesting to note that the necessary discontinuity has been provided for in ways other than critical concentration. For example, Joule (*Phil. Mag.*, 1844, **24**, 106) explains the periodic anodic dissolution of zinc amalgam in sulphuric acid as follows: the zinc dissolves smoothly until, at a certain critical *C.D.*, more sulphate ions are being discharged than can be replaced by diffusion. An oxide film then forms and oxygen is evolved. The stirring effect produced by the oxygen brings a layer of fresh solution, rich in sulphate ions, into contact with the electrode. Here, the discontinuity is provided by the stirring. This view is not capable of a very wide application, since in many cases (of which that described in the experimental portion of the present paper is the best example) no appreciable amount of gas is evolved.

Evans ("Metals and Metallic Compounds," Vol. 1, p. 382) suggests that periodic passivity in iron is due to the accumulation of hydrogen ions in the neighbourhood of the anode, due to the discharge of hydroxyl ions, and that the acid so produced activates the passive

electrode. It may be noted that inherent in this theory is the assumption that the acid does not activate the metal until a certain critical concentration is reached, or otherwise a state of equilibrium would be realised. But, in view of the fact that such hydrogen ions are produced only as a result of the formation of a protective film on the metal and also that they tend to migrate from the positively charged anode, it is difficult to imagine that the hydrogen ions would get to the electrode by diffusion against a potential gradient. The phenomena described in the experimental portion of the present paper take place equally well whether the electrolyte is hydrochloric acid, sodium chloride, or ammonium chloride, again suggesting the chlorine ion rather than the hydrogen ion as the active agent. In any case, there are numerous instances of the phenomenon occurring in alkaline solutions, and this view cannot explain periodicity at the cathode.

The former experiments on the anodic dissolution of copper in hydrochloric acid (J., 1926, 1538) seemed to indicate that the oxidic film was first deposited in an unstable state which in time reverted to a stable, poorly resistant film. The change in state of the film affords the necessary discontinuity. If this explanation were correct, the frequency would depend on the stability of the film and not on the rate of stirring, and it therefore seems probable that the changes observed in the film are due to the action of the hydrochloric acid. In a recent paper, Lillie (*Science*, 1928, 47, 593) discusses the analogies between the periodic passivity of iron immersed in nitric acid of certain concentrations and physiological periodicity, and maintains that the interval between the active periods "represents a temporary non-transmissive or 'refractory' period, during which the reactive molecules are to be regarded as assembling at the surface, and presumably there undergoing orientation or other change favorable to reaction." This view is identical with the unstable-film theory mentioned above, but the present experiments do not support any view based on a change occurring in the metal or in the film with which it is coated. It is evident that the cause of the activation lies in the solution and not in the electrode.

Periodic phenomena in electrolysis are encountered only between certain well-defined border-line conditions, and the idea of a critical concentration of some ion required to effect the change of the electrode from one state to the other is capable of extension to all the systems examined, both at the anode and at the cathode. Indeed, experiments on the periodic electrodeposition of metals through secondary reaction (J., 1927, 1077) afford strong independent support for the view, and are difficult to explain in any other way.

Physiologists use a similar view to explain the periodicity of breathing: respiration occurs every time the carbon dioxide content (*hydrogen-ion concentration*) of the blood reaches a threshold value. Although the older idea, that the heart-beat is caused by alternate reaction with or absorption of calcium and potassium ions, does not appear to be greatly favoured by physiologists, it may be pointed out that analogous mechanisms do exist. For example, in the electrolysis of mercury potassium cyanide solutions, under certain conditions the potassium liberated at the mercury cathode reacts alternately with water molecules and with the complex $Hg(CN)''_4$ ions or undissociated salt, the effect being a periodic evolution of hydrogen alternating with deposition of mercury. The supposition is here that reaction of potassium with the complex ions does not take place until the ions reach a certain critical concentration by diffusion. In colloid systems, critical concentrations of ions are required for coagulation, and such systems appear to be particularly favourable for periodic phenomena.

One experimental result appears to contradict the theory that has been developed. The temperature coefficient of the periods given by a rotating copper anode in 40% hydrochloric acid, determined by measuring the frequency at 30° and at 40°, was found to be 1·8 per 10°—a high value if the frequency is controlled entirely by a diffusion process. However, the difficulty of interpreting the temperature coefficient of a complicated series of chemical and physical processes is well known. The temperature coefficient of the heart-beat is anomalous (Bayliss, "General Principles of Physiology," p. 43).

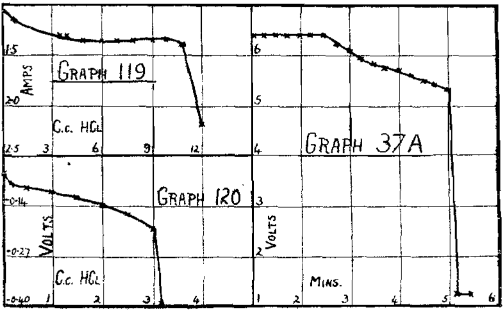
Experimental Evidence of Critical Concentrations.

If the fall of potential is due to the hydrochloric acid slowly reaching a critical concentration by diffusion in the neighbourhood of the anode, it should be possible to produce the same effect by adding hydrochloric acid directly to a permanently "passive" anode. This has been done. A copper anode was rotated at 120 r.p.m. in 15% hydrochloric acid, a *C.D.* of 300 milliamp./cm.^{2} being used. The film soon appeared and the *C.D.* fell to 147 milliamp./cm.^{2}, at which it remained constant, for the high *C.D.* is above the region of periodicity, the film remaining permanently. Hydrochloric acid (*d* 1·16) was added in small quantities at a time to the stirred liquid, and the amount of current passing was read after each addition. In Graph 119 (Fig. 4) the total current is plotted inversely against the number of c.c. of hydrochloric acid. Gradual addition of hydrochloric acid causes a slow fall in potential until a certain concentration is reached, whereupon the fall becomes

sudden. That this artificial process is identical with that occurring naturally in the periodic dissolution is evident by a comparison of Graph 119 with Graph 37A (Fig. 4) (reproduced from part of Graph 37; J., 1926, 1536), which shows the manner of fall of potential during one period.

Further evidence has been sought in the change from passive to active iron, the passivity being produced by purely chemical means. Previous work has shown that a change from the passive to the active state can generally be made to proceed periodically, whether the passivity is produced by chemical means or by anodic polarisation. A strip of electrolytic iron was rotated at 180 r.p.m.

FIG. 4.



in nitric acid (*d* 1·46), and successive small quantities of hydrochloric acid (*d* 1·16) were added at intervals. After each addition, the potential against a *N*-calomel electrode was measured by means of a string electrometer. The results are plotted in Graph 120 (Fig. 4) and show that here also activation occurs suddenly when a certain critical concentration of chlorine ions is reached.

From the form of the curves and from general considerations, it does not seem likely that *no* reaction occurs until the critical concentration is reached, but that the rate of reaction with a given ion increases very rapidly with the concentration of the ion until it becomes practically instantaneous. This is the significance of the critical concentration, just as in crystallisation the older view of the existence of a definite metastable limit has been replaced by the idea of a rapid increase in the number of nuclei with the degree of super-cooling (Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903).

Summary.

Experiments designed to elucidate the mechanism of periodic phenomena in electrolysis have been conducted by using a rotating anode, the system chosen for examination being the anodic dissolution of copper in hydrochloric acid. The frequency of the periods is independent of *C.D.* over a certain range and later decreases with increase of *C.D.* It is shown that this second stage is due to the accumulation of cuprous chloride at the electrode. The characteristic frequency (*i.e.*, that during the stage which is independent of *C.D.*) increases linearly with the rate of rotation of the anode and with the concentration of the hydrochloric acid. The periods are independent of the rate of formation of ions from the metal, but depend on the rate of supply of chlorine ions to the anode, and it appears that the chlorine ions have to accumulate to a certain *critical concentration before the film covering the anode during each* period can be dissolved : reaction in each pulse is complete and this gives rise to the periodicity. Direct evidence of the existence of such critical concentrations has been obtained by the progressive addition of hydrochloric acid to (*a*) copper rendered passive by anodic polarisation in hydrochloric acid, (*b*) iron rendered passive by concentrated nitric acid. A theory of anodic polarisation and its relation to passivity previously advanced is amplified.

The author is indebted to the Chemical Society and to the Trustees of the Dixon Fund of the University of London for grants which have assisted this work.

BEDFORD COLLEGE (UNIVERSITY OF LONDON),
REGENT'S PARK, N.W. 1. [*Received, March 16th*, 1929.]

CXXXVI.—*The Action of Potassium Cyanide on Chloroaldehydes.*

By FREDERICK DANIEL CHATTAWAY and HARRY IRVING.

THE action of potassium cyanide on an aqueous, an alcoholic, or an ammoniacal solution of a chloroacetaldehyde or of ααβ-trichlorobutaldehyde follows in every case a similar course; heat is evolved, hydrogen cyanide is liberated, and potassium chloride is formed together with an acid, an ester, or an amide containing one halogen atom less than the parent aldehyde. The reaction may be represented thus:

$$:CCl\cdot CHO \xrightarrow[H\cdot OH(OR)(NH_2)]{KCN} :CH\cdot CO\cdot OH(OR)(NH_2) + KCl + HCN.$$

Wallach (*Ber.*, 1873, **6**, 114) found that in ethyl-alcoholic solution ethyl dichloroacetate was yielded hy chloral and potassium cyanide. Ethyl monochloroacetate is similarly formed from dichloroacetaldehyde, and ethyl acetate from monochloroacetaldehyde.

The first product of the action of potassium cyanide on an alcoholic solution of butyl chloral hydrate (I) is an alkyl αβ-dichlorobutyrate (II) which loses hydrogen chloride so readily that, unless the reaction is carefully controlled, only an alkyl α-chlorocrotonate (III) is obtained (compare Wallach and Böhringer, *Annalen*, 1874, **173**, 301):

$$\underset{\text{(I.)}}{\begin{matrix} CHCl{\cdot}CH_3 \\ | \\ CCl_2{\cdot}CH(OH)_2 \end{matrix}} \xrightarrow[\text{ROH}]{\text{KCN}} \underset{\text{(II.)}}{\begin{matrix} CHCl{\cdot}CH_3 \\ | \\ CHCl{\cdot}CO_2R \end{matrix}} \xrightarrow{\text{KCN}} \underset{\text{(III.)}}{\begin{matrix} CH{\cdot}CH_3 \\ \| \\ CCl{\cdot}CO_2R \end{matrix}}$$

α-Chlorocrotonic acid, $CH_3{\cdot}CH{:}CCl{\cdot}CO_2H$, or α-chlorocrotonamide, $CH_3{\cdot}CH{:}CCl{\cdot}CO{\cdot}NH_2$, is similarly formed by the action of potassium cyanide upon an aqueous or ammoniacal solution of butyl chloral hydrate, but in these cases the loss of hydrogen chloride from the intermediate αβ-dichlorobutyric acid or amide is too rapid to permit of its isolation.

Since potassium cyanide acts similarly upon all the aliphatic chloroaldehydes studied, it seems certain that the nature of the reaction is the same in every case.

No satisfactory explanation of it has, however, yet been put forward. Wallach (*Ber.*, 1877, **10**, 2124), after many years work on the reaction, adopted a suggestion made by Victor Meyer (*ibid.*, p. 1740) that the process was one of simultaneous oxidation and reduction of the chloral molecule catalysed by hydrogen cyanide, the dichloroacetic acid being subsequently esterified when the reaction was carried out in alcohol:

$$\begin{matrix} CCl_3{\cdot}CHO \\ H_2{:}O \end{matrix} \longrightarrow CHCl_2{\cdot}CO{\cdot}OH + HCl \xrightarrow{\text{EtOH}} CHCl_2{\cdot}CO{\cdot}OEt.$$

This conclusion may be disregarded, since it is not chloral but chloral alcoholate that is concerned, and since the rate of esterification of dichloroacetic acid is comparatively slow.

Another explanation, put forward by Kötz (*J. pr. Chem.*, 1913, **88**, 531), assumes that the formation of chloral cyanohydrin is an essential part of the reaction. The strongest argument in favour of this assumption is the fact that reactions of the type under consideration are brought about only by alkaline cyanides.* Other

* Mercury cyanide crystallises unchanged after heating for several hours with an alcoholic solution of chloral hydrate, no ethyl dichloroacetate being formed.

similarly weak alkaline reagents simply hydrolyse the chloral *molecule to chloroform and a formate.*

On the other hand, many facts seem to indicate that the formation of a cyanohydrin is not a necessary step in the reaction but a secondary reaction due to the liberation of hydrogen cyanide in the primary one. For example, the action of potassium cyanide upon an alcoholic solution of chloral alcoholate is as violent as, or even more violent than, its action upon a similar solution of chloral cyanohydrin, and all conditions which favour the formation of cyanohydrin in the reaction hinder rather than promote the formation of an alkyl dichloroacetate. Again, the action of potassium cyanide upon the chloroaldehyde-ammonias in presence of excess of ammonia follows a course closely resembling that between potassium cyanide and the alcoholates, although cyanohydrin formation under the conditions appears unlikely. For example, the action of potassium cyanide upon chloral-ammonia, dissolved in alcohol saturated with ammonia, yields dichloroacetamide thus :

$$CCl_3\cdot CH(OH)\cdot NH_2 \xrightarrow[NH_3]{KCN} CHCl_2\cdot CO\cdot NH_2 + KCl + NH_4CN.$$

α-Chlorocrotonamide is similarly formed from butyl chloral-ammonia, the intermediate αβ-dichlorobutyramide, in presence of excess of ammonia, losing hydrogen chloride too rapidly to permit of its isolation.

In view of the unlikelihood of cyanohydrin formation in such cases, it seems more probable that the potassium cyanide first causes the *elimination of* hydrogen chloride from the aldehyde-hydrate, aldehyde-alcoholate, or aldehyde-ammonia, probably by the intermediate replacement of a chlorine atom by a cyanogen group, followed by a splitting off of the very slightly ionisable hydrogen cyanide, and leaves an unsaturated compound which by a familiar intramolecular rearrangement gives an acid, an ester, or an acid amide, thus :

$$:CCl\cdot CH{<}^{OH}_{OH(OR)(NH_2)} \xrightarrow{KCN} :C:C{<}^{OH}_{OH(OR)(NH_2)} \longrightarrow$$
$$:CH\cdot CO\cdot OH(OR)(NH_2);$$

or with trichlorobutaldehyde,

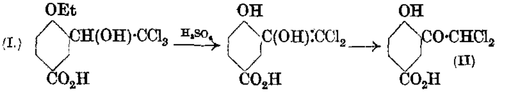
$$CHMeCl\cdot CCl_2\cdot CH{<}^{OH}_{OH(OR)(NH_2)} \xrightarrow{KCN} CHMeCl\cdot CCl:C{<}^{OH}_{OH(OR)(NH_2)}$$
$$\longrightarrow CHMeCl\cdot CHCl\cdot CO\cdot OH(OR)(NH_2) \xrightarrow{KCN}$$
$$CHMe:CCl\cdot CO\cdot OH(OR)(NH_2).$$

There are certain analogous reactions which, although they involve a similar elimination of hydrogen chloride followed by intramolecular rearrangement, can take place in the absence of an

alkaline cyanide. For example, when an aqueous solution of the sodium salt of a chlorolactic acid is boiled, carbon dioxide is evolved and sodium chloride is formed together with an aldehyde containing one chlorine atom less than the original acid (compare Reisse, *Annalen*, 1890, **257**, 331), the reaction without doubt taking the course

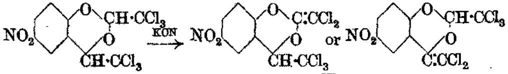
$$CCl_3\cdot CH{<}^{OH}_{CO\cdot ONa} \longrightarrow CCl_2{:}C{<}^{OH}_{CO\cdot OH} \longrightarrow CHCl_2\cdot \overset{O}{\overset{/\!/}{C}}\cdot CO\cdot OH \longrightarrow CHCl_2\cdot CHO.$$

Again, ωω-dichloro-2-hydroxyacetophenone-5-carboxylic acid (II) is formed when 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I) is heated for a short time with concentrated sulphuric acid (Chattaway and Calvet, J., 1927, 691):



(I.) (II)

The facility with which potassium cyanide can promote the elimination of hydrogen chloride is shown by its action on 6-nitro-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin (III), whereby one molecule of hydrogen chloride is removed, giving 6-*nitro*-2(or 4)-*dichloromethylene*-4(or 2)-*trichloromethyl*-1 : 3-*benzdioxin* (IV):



(III.) (IV.)

A similar elimination of hydrogen chloride from the second $>CH\cdot CCl_3$ group does not occur.

Other cases in which potassium cyanide fails to replace chlorine by cyanogen are well known. For example, potassium cyanide has little or no action upon monochloroacetal, $CH_2Cl\cdot CH(OEt)_2$ (compare Hesse, *Ber.*, 1897, **30**, 1441), αβββ-tetrachlorodiethyl ether, $CCl_3\cdot CHCl\cdot OEt$ (compare Busch, *Ber.*, 1878, **11**, 447), parachloral [2 : 4 : 6-tri(trichloromethyl)*cyclo*-1 : 3 : 5-trioxa-2 : 4 : 6-trimethylene] (Chattaway and Kellett, J., 1928, 2712), nor, as we have found, upon dichloroacetal, $CHCl_2\cdot CH(OEt)_2$, and 5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene.

EXPERIMENTAL.

The Action of Potassium Cyanide on Chloral Alcoholates.—The action of potassium cyanide on solutions of chloral alcoholates in

the corresponding alcohols is completed as rapidly as the reactants can be brought together, the time taken being apparently limited only by the violence of the reaction. The yields of the corresponding alkyl dichloroacetates are very large.

A solution of anhydrous chloral (1 mol.) in rather more than its own weight of the required alcohol was added as rapidly as possible to a suspension of finely powdered potassium cyanide (1·2 mols.) in the same alcohol, loss of alcohol by boiling being prevented by suitable cooling. After about 1 minute, water was added to dissolve the excess of potassium cyanide together with the potassium chloride formed. The ester, which then separated as a heavy lower layer, was washed repeatedly, first with a dilute solution of potassium hydroxide and then with water, freed from any traces of cyanohydrin by steam distillation, dried over calcium chloride, and fractionated. The following results were obtained :—Methyl dichloroacetate, b. p. 143° (yield, 84%); ethyl dichloroacetate. b. p. 157° (yield, 88%).

n-*Propyl dichloroacetate*, b. p. 176° (yield, 70%) (Found : Cl, 41·4. $C_5H_8O_2Cl_2$ requires Cl, 41·5%), and *allyl dichloroacetate*, b. p. 175·5° (yield, 64%) (Found : Cl, 42·0. $C_5H_6O_2Cl_2$ requires Cl, 42·0%), were similarly prepared, a solution of chloral hydrate in the required alcohol being used.

When potassium cyanide is allowed to act upon an alcoholic solution of chloral cyanohydrin, or when the reaction between potassium cyanide and chloral alcoholate is carried out under conditions which favour its formation (such, for example, as the slow addition of the cyanide to the solution of the chloral alcoholate at a fairly low temperature), the yield of alkyl dichloroacetate is greatly reduced. For example, when potassium cyanide (1 mol.) was added in small portions to a well-stirred solution of chloral ethyl alcoholate (1 mol.) in ethyl alcohol at such a rate that the temperature was kept at 25—30°, only a 43% yield of ethyl dichloroacetate was obtained, and much chloral cyanohydrin was isolated from the higher-boiling fractions of the product.

The action of potassium cyanide upon a solution of chloral cyanohydrin in ethyl alcohol, though very vigorous and accompanied by a considerable evolution of heat, was found not to commence immediately, was much less violent than when chloral alcoholate was used, and gave a smaller yield of ethyl dichloroacetate (61%).

The Action of Potassium Cyanide upon Dichloroacetaldehyde Ethyl Alcoholate : Formation of Ethyl Monochloroacetate.—64 G. of dichloroacetaldehyde ethyl alcoholate (1 mol.) were added as rapidly as practicable to 29 g. of finely powdered potassium cyanide (1 mol.)

suspended in 40 g. of ethyl alcohol at 20°. After 5 minutes, water was added to the red product, and the heavy lower layer which separated was washed with a dilute solution of potassium carbonate and with water, dried rapidly over calcium chloride, and fractionated, giving 19·9 g. of ethyl chloroacetate, b. p. 143·5—145° (yield, 38%). This was further identified by conversion into chloroacetamide, m. p. 117° (Found: Cl, 37·85. Calc. for C_2H_4ONCl: Cl, 38·0%).

The Action of Potassium Cyanide on Monochloroacetaldehyde.—(1) *In alcoholic solution.* 7 G. of powdered potassium cyanide (1 mol.) were added to a solution of 8 g. of monochloroacetaldehyde (1 mol.) in 30 c.c. of ethyl alcohol. A brisk reaction commenced at once, hydrogen cyanide was evolved and the temperature rose to the boiling point of the alcohol while the solution became deep red. After 5 minutes, water was added, and the oily liquid produced was washed several times with a strong solution of calcium chloride (50 g. in 50 c.c. of water) to remove alcohol, dried, and fractionated; ethyl acetate, identified by its smell and boiling point, 76—79°, was obtained, the yield being not more than 10% of the theoretical owing to loss in the process of isolation.

(2) *In aqueous solution.* 8·5 G. of potassium cyanide (1 mol.) were added to a solution of 10 g. of monochloroacetaldehyde in 50 c.c. of water. The temperature rose somewhat, but as there was no marked action the solution was boiled for 2 hours under reflux; it was then made strongly alkaline with potassium hydroxide and evaporated to dryness. The dry powdered mixture of potassium salts was distilled with concentrated sulphuric acid, acetic acid being obtained, b. p. 115—117° after several fractionations (yield, not more than 10%).

Owing to the great difficulty of preparing monochloroacetaldehyde larger quantities than the above could not be used.

The Action of Potassium Cyanide on Butyl Chloral Hydrate in Alcoholic Solution: Isolation of Ethyl αβ-Dichlorobutyrate, Ethyl α-Chlorocrotonate, and Butyl Chloral Cyanohydrin.—Unless the violence of the reaction is moderated when potassium cyanide is added to an alcoholic solution of butyl chloral hydrate, the only ester which is found in the product is ethyl α-chlorocrotonate (compare Wallach, *Annalen*, 1874, **173**, 301). When, however, the temperature is not allowed to rise during the reaction, ethyl αβ-dichlorobutyrate, which is the first product of the action, may be isolated.

11 G. of finely powdered potassium cyanide (1 mol.) were added in small portions to a mechanically stirred solution of 32·5 g. of butyl chloral hydrate (1 mol.) in 150 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (2 hours); the

solution became pale yellow and potassium chloride (11·9 g. Theoretical for 1 mol. KCl, 12·4 g.) separated. Strong brine was added to the filtrate until two layers formed and, after the whole had been made slightly acid with hydrochloric acid, the lower layer was separated, dried rapidly over calcium chloride, and distilled under reduced pressure (15 mm.) until a white solid which condensed in the receiver ceased to come over.

By repeated fractional distillation under reduced pressure, the liquid portion of the distillate was separated into ethyl α-chlorocrotonate (7 g.), b. p. 85°/35 mm. and 176°/760 mm. (Found: Cl, 23·9. Calc.: Cl, 23·9%), and ethyl αβ-dichlorobutyrate (4 g.), b. p. 97°/35 mm. and 180—200°/760 mm. with marked decomposition (compare Michael and Brown, *Amer. Chem. J.*, 1887, **9**, 274) (Found: Cl, 38·1. Calc.: Cl, 38·3%).

In the fractionation of the distillate, after distillation of the two esters a white solid residue of *butyl chloral cyanohydrin* was left. This crystallised from boiling water, in which it was moderately easily soluble, in colourless, shining, unctuous plates, m. p. 101—102°, and on prolonged boiling with concentrated hydrochloric acid was hydrolysed to ββγ-trichloro-α-hydroxyvaleric acid, m. p. 140·5° (compare Pinner and Klein, *Ber.*, 1878, **11**, 1488) (Found: Cl, 52·5; N, 7·1. $C_5H_6ONCl_3$ requires Cl, 52·5; N, 7·0%).

Ethyl αβ-dichlorobutyrate loses hydrogen chloride with great ease even at the ordinary temperature, giving ethyl α-chlorocrotonate. A specimen which had been kept for 2 days in a stoppered bottle gave Cl, 36·5%.

This elimination of hydrogen chloride is greatly accelerated by the presence of potassium cyanide as shown by the following experiment, which explains why ethyl αβ-dichlorobutyrate is not normally found among the products of the action of potassium cyanide upon an alcoholic solution of butyl chloral hydrate. To 5 g. of ethyl αβ-dichlorobutyrate (1 mol.), diluted with 20 c.c. of alcohol, were added 1·7 g. of powdered potassium cyanide (1 mol.). After 10 minutes, the reaction mixture was poured into water and the ester was washed with water, dried, and fractionated, 3 g. of ethyl α-chlorocrotonate, b. p. 176°, being obtained (yield, 75%).

In carrying out the reaction between potassium cyanide and butyl chloral hydrate it is not practicable to avoid the formation of cyanohydrin by adding the butyl chloral alcoholate to the cyanide, since the alkyl α-chlorocrotonate produced by the action of potassium cyanide on the alkyl αβ-dichlorobutyrate first formed, itself reacts with potassium cyanide to give viscous yellow products of indefinite composition (compare Claus, *Annalen*, 1878, **191**, 33).

For this reason it is essential to avoid an excess of potassium

cyanide; by using, however, the correct amount of cyanide, a very satisfactory yield of any alkyl α-chlorocrotonate can be obtained provided that the temperature is not allowed to rise above 20°.

19 G. of finely powdered potassium cyanide (2 mols.) were added to a mechanically stirred solution of 29 g. of butyl chloral hydrate (1 mol.) in 150 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (3—4 hours). Hydrogen cyanide was evolved freely, especially towards the end of the reaction, and on filtration 21·5 g. of potassium chloride were obtained (theoretical for 2 mols. KCl, 21·7 g.). The filtrate was diluted with water, and the ethyl α-chlorocrotonate distilled in steam, dried over calcium chloride, and fractionated, 22 g., b. p. 176°, being obtained (yield, 90%) (Found: Cl, 23·9. Calc.: Cl, 23·9%).

Steam distillation and subsequent fractionation under reduced pressure are necessary to remove traces of cyanohydrin with which the alkyl α-chlorocrotonates, especially the higher-boiling ones, are contaminated. Several esters were prepared thus: Methyl α-chlorocrotonate, b. p. 161° (yield, 85%) (Found: Cl, 26·4. Calc.: Cl, 26·4%), *n*-propyl α-chlorocrotonate, b. p. 191° (yield, 67%) (Found: Cl, 22·0. Calc.: Cl, 21·8%), *n*-butyl α-chlorocrotonate, b. p. 205° (yield, 70%) (Found: Cl, 20·2. Calc.: Cl, 20·5%).

When potassium cyanide is added to an alcoholic solntion of butyl chloral hydrate the hydrogen cyanide liberated reacts with the unchanged aldehyde, giving butyl chloral cyanohydrin, and by stopping the reaction when half the theoretical amount of cyanide has been added some 50% of the original aldehyde can be isolated as cyanohydrin. On account of its sparing solubility, this actually separates when the reaction is carried out in aqueous solution (*q.v.*).

Butyl chloral cyanohydrin will itself react with potassium cyanide in alcoholic solution, giving ultimately an alkyl α-chlorocrotonate. 9 G. of powdered potassium cyanide (2 mols.) were added in small portions to a mechanically stirred solution of 14 g. of butyl chloral cyanohydrin (1 mol.) in 100 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (2½ hours). 10·1 G. of potassium chloride (theoretical for 2 mols. of KCl, 10·3 g.) and ethyl α-chlorocrotonate, which was isolated and purified in the usual way (8·5 g., b. p. 176°; yield, 85%), were obtained.

The Action of Potassium Cyanide upon Butyl Chloral Hydrate in Aqueous Solution: Formation of α-Chlorocrotonic Acid and Butyl Chloral Cyanohydrin.—13·5 G. of potassium cyanide (2 mols.) were added to a solution of 19·5 g. of butyl chloral hydrate (1 mol.) in 500 c.c. of water at 40°. The temperature rose at once to 47° as the

cyanide dissolved, and butyl chloral cyanohydrin separated as a heavy, colourless, oily liquid. After warming at 50° for a few minutes, the whole was cooled to 0° and the cyanohydrin extracted with chloroform (obtained, 4·1 g.; m. p. 101—102°). The remaining solution was made strongly acid with sulphuric acid, and the α-chlorocrotonic acid (6·2 g.) extracted with ether; it crystallised from low-boiling petroleum in long, slender, colourless needles m. p. 98·5—99° (Found: Cl, 39·8. Calc.: Cl, 39·8%).

The Action of Potassium Cyanide on Chloral-ammonia: Formatio of Dichloroacetamide.—13 G. of powdered potassium cyanid (1 mol.) were added to 33 g. of chloral-ammonia (1 mol.) suspended i 50 c.c. of aqueous ammonia (*d* 0·880) at 15°. A vigorous reactio started almost at once and the temperature rose rapidly to 70°; clear solution was then obtained from which, on cooling, dichlor acetamide, m. p. 98·5—99·0°, separated (yield, 24 g.; 93%) (Found Cl, 55·5. Calc.: Cl, 55·5%).

A similar vigorous reaction ensued when 50 c.c. of aqueo ammonia (*d* 0·880) were added to an intimate mixture of 13 g. potassium cyanide (1 mol.) and 33·5 g. of chloral hydrate (1 mol. The yield of dichloroacetamide was, however, only 50% of tl theoretical, part of the chloral hydrate being converted into chlor form and formate by the ammonia.

The Action of Potassium Cyanide on Butyl Chloral-ammonia Formation of α-Chlorocrotonamide.—19·5 G. of butyl chloral hydra (1 mol.), when added to 50 c.c. of aqueous ammonia (*d* 0·88 immediately dissolved, giving a clear solution from which but chloral-ammonia (m. p. 62°) separated in a few seconds as a hea colourless liquid. The whole was at once cooled in a freez mixture and saturated with dry ammonia gas; it was then warm to 10° and 14 g. of powdered potassium cyanide (1 mol.) were add The temperature rose to 35° and a brisk reaction commenced wh was completed by heating to 70°. On cooling, α-chlorocrotonam (11·2 g.), m. p. 113·5°, separated (yield, 93%) (Found: Cl, 29 N, 11·7. Calc.: Cl, 29·7; N, 11·7%).

Potassium cyanide has little or no action upon dichloroace 20 G. of dichloroacetal (1 mol.) were mixed with 7 g. of potass cyanide (1 mol.). No action appeared to take place even after hours, so the mixture was heated at 120° for 2 hours. The col of the acetal darkened, but on filtration and fractionation 18 g dichloroacetal, b. p. 183°, were recovered unchanged.

2 G. of 5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyet benzene were dissolved in 30 c.c. of alcohol and boiled with 1·2 g potassium cyanide (3 mols. + excess) for 2½ hours. No reac appeared to take place and from the diluted acidified mixture

original acid, m. p. 198° (from alcohol), separated unchanged as a granular precipitate.

The Action of Potassium Cyanide on Chloral Diacetate.—When potassium cyanide was added to chloral diacetate, $CCl_3{\cdot}CH(OAc)_2$, a violent action occurred and a black coked solid was formed from which nothing could be isolated.

15·5 G. of powdered potassium cyanide (1·5 mols.) were added in small portions to 40 g. of chloral diacetate (1 mol.) diluted with 60 g. of ethyl alcohol. A violent reaction ensued at each addition of the cyanide, hydrogen cyanide was evolved, and the temperature rose rapidly to the boiling point of the alcohol. After 5 minutes, water was added to the reaction product; the mixture of ethyl acetate and ethyl dichloroacetate produced was washed with water, dried, and fractionated, 20 g. of ethyl dichloroacetate being obtained (yield, 80%). A similar experiment in methyl-alcoholic solution gave 17·5 g. of methyl dichloroacetate (yield, 76%).

The Action of Potassium Cyanide on Butyl Chloral Hydrate in Benzene.—In 1874, Wallach found that a substance $C_7H_4O_3NCl_9$, m. p. 123°, was formed by the action of potassium cyanide under certain conditions upon a solution of chloral hydrate in benzene: to this substance a heterocyclic structure has been assigned by Crowther, McCombie, and Reade (J., 1914, **105**, 933). A similar *compound*, probably possessing the structure 6-keto-2 : 4 : 7-tri-(ααβ-trichloropropyl)*cyclo*-2 : 4 : 6 : 7-tetramethylene-1 : 3 : 5-dioxa-imine, $O{<}^{CH(CCl_2{\cdot}CHMeCl){\cdot}CO{\cdot}NH}_{CH(CCl_2{\cdot}CHMeCl)\text{———}O}{>}CH{\cdot}CCl_2{\cdot}CHMeCl$, is yielded by butyl chloral hydrate.

7·8 G. of powdered potassium cyanide (1·2 mols.) were added to a solution of 58 g. of butyl chloral hydrate (3 mols.) in 150 c.c. of benzene, and the mixture kept at the ordinary temperature with occasional shaking for 10 days. The solution darkened in colour but no visible reaction occurred, so the whole was filtered. The benzene was allowed to evaporate slowly from the filtrate. The viscous residue was dissolved in a little cold ligroin, in which it was very easily soluble; a bulky white solid slowly separated. This, after being washed with a little ligroin, crystallised from boiling light petroleum (b. p. 80—100°), in which it was moderately easily soluble, as a friable, colourless, microcrystalline powder, m. p. 99·5—100·5° (Found: C, 28·2; H, 2·9; N, 2·5; Cl, 57·7; *M*, cryoscopic in benzene, 548, 545. $C_{13}H_{16}O_3NCl_9$ requires C, 28·6; H, 2·8; N, 2·6; Cl, 57·7%; *M*, 553).

When solid butyl chloral hydrate (3 mols.) is added to a saturated aqueous solution of potassium cyanide (1 mol.) at 0°, the clear solution first formed soon deposits a colourless oily liquid which

later solidifies. The product appears to be a mixture of the above substance with butyl chloral cyanohydrin, but a complete separation could not be effected.

The Action of Potassium Cyanide upon 6-*Nitro*-2 : 4-*bis(trichloromethyl)*-1 : 3-*benzdioxin* : *Formation of* 6-*Nitro*-2(or 4)-*trichloromethyl*-4(or 2)-*dichloromethylene*-1 : 3-*benzdioxin*.—6·5 G. of powdered potassium cyanide were added to a solution of 41 g. of 6-nitro-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin in 100 c.c. of ethyl alcohol. On heating, hydrogen cyanide was evolved. After refluxing on a water-bath for ½ hour to complete the reaction, the alcohol was distilled off in a current of steam; 6-*nitro*-2(or 4)-*trichloromethyl*-4(or 2)-*dichloromethylene*-1 : 3-*benzdioxin* was left suspended in the water as a crystalline residue. After being washed with water, it crystallised from boiling alcohol, in which it was easily soluble, in colourless, elongated, rhombic prisms, m. p. 136·5° (Found : Cl, 46·7. $C_{10}H_4O_4NCl_5$ requires Cl, 46·7%).

The substance does not readily form an addition compound with bromine.

THE QUEEN'S COLLEGE, OXFORD. [*Received, February* 23*rd*, 1929.]

CXXXVII.—*The Reactions of the Halogens with Carbon Sulphidoselenide.*

By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and PERCY LUCOCK ROBINSON.

IN continuation of previous work (this vol., p. 56) carbon sulphido selenide has been found to react readily and exothermally witl chlorine and bromine. It does not react with iodine, even at 120 in sealed tubes, and although iodine dissolves in the liquid, it ma be completely removed by extraction with aqueous caustic soda.

As was anticipated, the reactions with chlorine and bromine sho some resemblance to the corresponding reactions of carbon disulphid Whereas carbon disulphide yields with chlorine thiocarbonyl tetra chloride, $CSCl_4$ (Klason, *Ber.*, 1887, **20**, 2377), and with bromin carbon disulphotetrabromide, CS_2Br_4 (Hell and Ureck, *Ber.*, 187 **9**, 788), carbon sulphidoselenide on chlorination at the ordinar temperature gives thiocarbonyl tetrachloride and selenium tetr chloride, and with bromine it yields *thiocarbonyl tetrabromide* (appa ently hitherto unknown) and selenium tetrabromide, or, und certain conditions, a solid intermediate *compound*, $C_2S_2SeBr_8$.

Aqueous solutions of the halogen acids do not react with carbo sulphidoselenide even after several hours' heating at 120°.

EXPERIMENTAL.

Reactions with Chlorine.—A solution of carbon sulphidoselenide in carbon tetrachloride, when saturated with chlorine, deposited a fine white solid which, when filtered, washed with carbon tetrachloride, and dried on a porous plate in a desiccator, was very hygroscopic and fumed continuously on exposure to the air (Found : Se, 34·9 ; Cl, 65·0. Calc. for $SeCl_4$: Se, 35·8 ; Cl, 64·2%).

Carbon sulphidoselenide (20 c.c.) suspended in water was treated with a slow current of chlorine. After some time a white precipitate was formed which slowly dissolved to give a clear supernatant solution. When the solution had been kept saturated with chlorine for 48 hours, the residual liquid (20 c.c.) was separated, washed with aqueous caustic soda, dried with calcium chloride, and distilled. It yielded a bright yellow, oily liquid, b. p. 147—149°, having a penetrating and disagreeable smell (Found : C, 6·5 ; S, 16·8 ; Cl, 75·8. Calc. for $CSCl_4$: C, 6·5 ; S, 17·2 ; Cl, 76·3%). Vapour-density measurements by Dumas's method gave values for the molecular weight of 210 at 170° and 198 at 200° (Calc. for $CSCl_4$, 186·0).

The density of the liquid, determined in a 10 c.c. glass pyknometer, was $d_{4^\circ}^{20^\circ}$ 1·6996 ; $d_{4^\circ}^{25^\circ}$ 1·6923. By using the method of capillary rise in three tubes, the mean value of the surface tension at 20° was found to be $\gamma = 35{\cdot}02$ dynes/cm., whence the molecular parachor, $M\gamma^{1/4}/D$, is 266·1. The value calculated for thiocarbonyl tetrachloride, assuming the mercaptan structure, is 4·8 (C) + 46·5 (S) + 217·2 (4 × Cl) = 268·5 ; and the agreement of this figure with the value found clearly confirms the formula $CCl_3{\cdot}S{\cdot}Cl$.

Reactions with Bromine.—Addition of excess of bromine to carbon sulphidoselenide dissolved in carbon tetrachloride yielded an orange-yellow precipitate which was filtered off, washed with carbon tetrachloride, and dried in a desiccator (Found : Se, 19·1 ; Br, 81·0. Calc. for $SeBr_4$: Se, 19·8 ; Br, 80·2%) ; it fumed continuously in air and was extremely hygroscopic, forming, when exposed to moist air for a few minutes, a yellow oil.

Carbon sulphidoselenide (20 c.c.) was suspended in water, and bromine (70 c.c.) was added, as required for the reaction $CSSe + 4Br_2 \longrightarrow CSBr_4 + SeBr_4$. The viscous oil formed (35 c.c.), after being kept under water for 2 days, washed with aqueous caustic soda, and dried over calcium chloride, yielded a clear, red liquid with a strong smell resembling that of yellow phosphorus. The liquid distilled mainly between 155° and 165°, but distillation, even under reduced pressure, caused progressive decomposition, so that free bromine was found in the head fraction and a white solid separated in the residue. This solid, recrystallised from aqueous

alcohol, had m. p. 90·0° (Found: C, 3·5; Br, 96·2. Calc. for CBr_4 : C, 3·6; Br, 96·4%).

A quantity of the red oil, which had not been distilled, when washed thoroughly with aqueous caustic soda and dried was considered to be reasonably pure (Found: C, 3·5; S, 9·4; Br, 87·4. $CSBr_4$ requires C, 3·3; S, 8·8; Br, 87·9%). The density determined in pyknometers was $d_{4°}^{20°}$ 3·0240, and the surface tension determined by the method of capillary rise was $\gamma_{20°} = 47{\cdot}74$ dynes/cm. From these data the molecular parachor $M\gamma^{\frac{1}{4}}/D = 316{\cdot}4$, in reasonable agreement with the value 323·3 calculated for the formula $CBr_3{\cdot}S{\cdot}Br$.

Carbon sulphidoselenide (10 c.c.), suspended in water, was treated with bromine (20 c.c.), and the thick oil was kept for several hours. It then set to a solid which crystallised from benzene as a fine white substance (54 g.) having a strong phosphorus-like smell (Found: C, 3·7; S, 10·0; Se, 12·2; Br, 74·9. $C_2Br_6S_2Se$ requires C, 3·7; S, 9·9; Se, 12·2; Br, 74·2%). It would appear that this substance is formed according to the reaction $2CSSe + 5Br_2 \longrightarrow C_2S_2SeBr_6 + SeBr_4$. Cryoscopic measurements of the molecular weight in benzene gave low results, suggesting that dissociation occurs in solution. The solid distils under reduced pressure to form a dark red oil which has the same composition as the original solid but does not crystallise unless kept under water. It seems likely that this substance exists in two forms, one of which is liquid; and this view is supported by its behaviour on melting. If the solid is slowly and steadily heated, it melts sharply at 90·0°, but if it is maintained at a lower temperature for some minutes it will liquefy slowly even at 78°.

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [Received, April 3rd, 1929.]

CXXXVIII.—*The Reactions of Nitrosulphony Chlorides. Part I. The Reaction of Hydrazin Hydrate with o-Nitrosulphonyl Chlorides.*

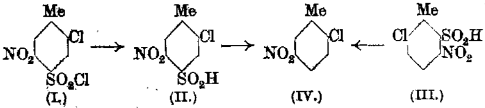
By ARTHUR THURLBY DANN and WILLIAM DAVIES.

THE reaction between hydrazine hydrate and 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (I) in the cold gives the primary *hydrazi* $R{\cdot}SO_2{\cdot}NH{\cdot}NH_2$, but from the warm mixture more than 90% of th *sulphinic acid* and the theoretical quantity of nitrogen required t

the equation $2R{\cdot}SO_2Cl + 2NH_2{\cdot}NH_2,H_2O = 2R{\cdot}SO_2H + N_2 + 2H_2O + NH_2{\cdot}NH_2,2HCl$ are obtained. The hydrazide decomposes in the presence of hot aqueous hydrazine or dilute hydrochloric acid to form the sulphinic acid and the theoretical quantity of nitrogen.

It is known (Curtius and Lorenzen, *J. pr. Chem.*, 1898, **58**, 166) that benzenesulphonhydrazide is decomposed by boiling water or aqueous alkali, benzenesulphinic acid and other organic substances being produced. As there is no evidence of ring formation with *o*-nitrobenzenesulphonhydrazides, the almost quantitative production of the *o*-nitrosulphinic acid is probably due to the activating or chemical effect of the nitro-group. This influence is well shown in the properties of the *o*-nitrosulphinic acids themselves. 2-*Chloro-5-nitro-*p*-toluenesulphinic acid* (II) has been kept almost unchanged for 7 years at room temperature. In hot pyridine (and in other hot solvents), however, it loses sulphur dioxide with the production of 2-chloro-5-nitrotoluene (IV) in 77% yield; under these conditions, naphthalene-β-sulphinic acid gives but 6·2% of naphthalene, and the chlorobenzene produced from *p*-chlorobenzenesulphinic acid can be detected only by its odour. 6-Chloro-3-nitro-*o*-toluenesulphinic acid (III) is so unstable that attempts to prepare it always result in the formation of (IV) in good yield (65%). *o*-Nitrobenzenesulphinic acid is of the same order of stability as (II).

m- and *p*-Nitrosulphinic acids are produced with much more difficulty than the *o*-isomeride by the action of hydrazine hydrate on the sulphonyl chloride; the difference is sufficiently great to enable an easy separation of at least one *o*-nitrosulphonyl chloride (as the sulphinic acid) from its position isomerides to be effected.



(I.) (II.) (IV.) (III.)

The product obtained by the addition of *o*- or *p*-nitrobenzoyl chloride to hydrazine hydrate contains both the primary and the secondary hydrazide; when the order of addition is reversed, the secondary hydrazide alone is formed (compare Naegli and Stefanovitsch, *Helv. Chim. Acta*, 1928, **11**, 636). In contrast with this behaviour, nitrosulphonyl chlorides have never in our experience given a secondary nitrosulphonhydrazide by direct reaction with hydrazine hydrate. Curtius and Lorenzen (*loc. cit.*), however, who dissolved their benzenesulphonyl chloride in alcohol, allude to the direct production of the secondary benzenesulphonhydrazide. It is evident that the presence of the nitro-group in the molecule makes

both the nitrosulphonyl chlorides and the nitrosulphinic acids anomalous, and the study of the properties of these substances is being continued.

EXPERIMENTAL.

The preparation of 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (I) (Davies, J., 1921, **119**, 860) is much simplified by the direct nitration of the crude undistilled monochlorination product from *p*-toluenesulphonyl chloride. The nitration mixture is washed with water and the mixture of sulphonyl chlorides is dried and crystallised from petroleum (b. p. 80—100°), the yield of (I) being 65% by weight of the original *p*-toluenesulphonyl chloride.

*Reaction between 2-Chloro-5-nitro-*p*-toluenesulphonyl Chloride and Hydrazine Hydrate.*—(I) *The sulphonyl chloride added to the hydrazine hydrate.* A solution of the sulphonyl chloride (21·6 g., 1 mol.) in benzene (30 c.c.) is added during 10 minutes to hydrazine hydrate (10 g. of 100%, 2½ mols.) in absolute alcohol (40 c.c.) with thorough shaking and intermittent cooling, but the temperature is allowed to reach 40°; a brisk evolution of nitrogen then occurs. After 4 hours, the precipitate of sulphinic acid is collected, stirred with cold dilute hydrochloric acid (60 c.c.), dissolved in dilute sodium hydroxide solution, and recovered (16·5 g., 87·6% yield), m. p. 129—131°.

(2) *The hydrazine hydrate added to the sulphonyl chloride.* The sulphonyl chloride (20 g.) is dissolved in ether or benzene (70 c.c.), and the hydrazine hydrate (without solvent) added in the cold. The precipitate is collected and heated with a little water, and the sulphinic acid purified as described above. Yield, 17 g. (97·5%); m. p. 125—128°.

Estimation of the nitrogen produced in the reaction. The sulphonyl chloride (0·4091 g.) in about 3 c.c. of benzene was mixed with 0·17 c.c. of hydrazine hydrate and 2 c.c. of alcohol and warmed, the usual apparatus, consisting of a small flask, a small tube, and a nitrometer, being employed. 17·61 C.c. of nitrogen (measured at 17° and 756 mm.) were obtained, corresponding to 0·49 mol. of nitrogen per mol. of sulphonyl chloride. In another experiment the nitrogen was shown, by sparking with oxygen, to be free from hydrogen. The product did not contain an amino-group, and ammonia was not produced in the reaction.

2-*Chloro-5-nitro-*p*-toluenesulphinic acid* (II) consists of very pale yellow needles, m. p. 131·5° (Found: C, 35·7; H, 2·8; N, 5·95, 6·05, 6·1; Cl, 15·4; equiv., 238·8; *M*, cryoscopic in phenol, 215, 219. $C_7H_6O_4NClS$ requires C, 35·6; H, 2·5; N, 6·0; Cl, 15·1%; *M* and equiv., 235·5). It is very soluble in the common organic solvents except light petroleum, readily soluble in hot and sparingly soluble in cold water, from which it is almost entirely precipitated by the

addition of concentrated hydrochloric acid. When the sulphinic acid (10 g.) is heated with pyridine (50 c.c.) on the water-bath for 50 hours, and the product diluted with water, 2-chloro-5-nitrotoluene (m. p. 44°; 5·0 g.) is obtained; the yield is increased to 5·6 g. (77%) by steam distillation after acidification of the filtrate (Found: C, 49·2; H, 3·4. Calc.: C, 48·9; H, 3·6%).

*2-Chloro-5-nitro-*p*-tolylmethylsulphone* is made from the sulphinic acid in small yield by methylation with methyl sulphate and sodium hydroxide, but in 50% yield together with only a small quantity of 2-chloro-5-nitrotoluene by shaking in the cold a suspension of the silver salt in methyl alcohol–methyl iodide for several hours. It separates from alcohol in colourless needles, m. p. 145—146°, and is extremely stable and difficult to oxidise completely either in a combustion tube or with nitric acid (Found: C, 37·9; H, 3·3; N, 5·7, 5·8. $C_8H_8O_4NClS$ requires C, 38·5; H, 3·2; N, 5·6%).

o-Nitrobenzenesulphinic acid is produced in 80% yield by method (1) above, the temperature being allowed to reach 60°; it is extracted from the hydrochloric acid solution with ether and obtained in thick, light yellow crystals, m. p. 138—139° (Claasz, *Annalen*, 1911, **380**, 311, gives m. p. 134°). The silver salt and methyl-alcoholic methyl iodide give the sulphone, m. p. 105° (compare Claasz, *Ber.*, 1912, **45**, 1020, 1023).

The Production of Nitrosulphonhydrazides.—*2-Chloro-5-nitro-*p*-toluenesulphonhydrazide.* A solution of the corresponding sulphonyl chloride (21·6 g.; 1 mol.) in benzene (65 c.c.) at 0° is very slowly added with stirring to hydrazine hydrate (10 g.; 2½ mols.) in absolute alcohol (50 c.c.) in a freezing mixture, the temperature being kept below 3°. After ½ hour, the precipitate is collected, washed with alcohol, well stirred with cold water until it is free from chloride, and dried in a vacuum over phosphoric oxide (yield, 20·8 g., 98%). The *sulphonhydrazide* forms colourless felted needles, m. p. 110—113° with brisk effervescence (Found: N, 15·95, 15·8. $C_7H_8O_4N_3ClS$ requires N, 15·8%). It is soluble in dilute acids and alkalis, practically insoluble in cold water and cold alcohol, slightly soluble in hot alcohol. It is unstable to heat, especially in hydroxylic solvents, but can be recrystallised by adding it to boiling methyl alcohol and rapidly decanting or filtering the solution into a cold vessel.

In hot alcoholic solution the hydrazide reacts with salicylaldehyde and cinnamaldehyde to form salicylidene- and cinnamylidene-azine, m. p. 216° and 166°, respectively. There is, however, evidence of the formation of the sulphonhydrazones, but these compounds are difficult to obtain pure when made in this medium. A warm anisole solution of the hydrazide and cinnamaldehyde give *cinnamaldehyde-*

*2-chloro-5-nitro-*p-*toluenesulphonhydrazone*, dark red leaves, m. p. 95°. The melting point rises with keeping (Found: N, 11·4, 11·3. $C_{16}H_{14}O_4N_3ClS$ requires N, 11·1%). The formation of this hydrazone, the fact that the hydrazide cannot be obtained pure from methyl alcohol rich in acetone, and the reduction of Fehling's solution in the cold all indicate that the constitution of the hydrazide is normal.

o-*Nitrobenzenesulphonhydrazide* is relatively unstable. The temperature should be kept below 0° during its preparation, and the sulphonhydrazide, which is fairly readily soluble in water, should be washed with sodium acetate solution. In this way almost colourless prisms, m. p. 101° (decomp.), are obtained in 82% yield (Found: N, 19·0. $C_6H_7O_4N_3S$ requires N, 19·35%). Claasz (*Ber.*, 1911, **44**, 1417) obtained from the action of aqueous alkali and hydrazine on *o*-nitrobenzenesulphonyl chloride exclusively potassium *o*-nitrobenzenesulphonate and azimidol.

*6-Chloro-4-nitro-*o-*toluenesulphonhydrazide*, colourless needles, m. p. 127°, and *2-chloro-6-nitro-*p-*toluenesulphonhydrazide*, m. p. 125°, plates, moderately easily soluble in cold alcohol, are both prepared in the usual way in excellent yield (Found respectively: N, 16·0, 16·0. $C_7H_8O_4N_3ClS$ requires N, 15·8%).

The Action of o-*Nitrobenzoyl Chloride on Hydrazine Hydrate.*—*o*-Nitrobenzoyl chloride (9·3 g., 1 mol.), dissolved in benzene (25 c.c.), is slowly added with vigorous stirring to hydrazine hydrate (5·1 g., 2 mols.) in benzene (30 c.c.). The precipitate is collected when cold and extracted twice with boiling water (50 c.c.), from which o-nitrobenzoylhydrazide (1·3 g.), identified by comparison with an authentic specimen, crystallises on cooling. The precipitate insoluble in water crystallises from nitrobenzene in minute needles (m. p. 298°, 5·8 g.), which become brown on prolonged exposure to light (Found: C, 50·8; H, 3·1; N, 17·4. Calc. for $C_{14}H_{10}O_6N_4$: C, 50·9; H, 3·0; N, 17·0%). This *NN'*-di-*o*-nitrobenzoylhydrazine is recognised as such by its inertness to cold Fehling's solution and by its inability to form hydrazones. It is undoubtedly the substance (m. p. higher than 250°) prepared from the *o*-nitrobenzoylhydrazone of acetoacetic ester (Beilstein, "Organische Chemie," IVth edition, vol. IX, p. 375).

p-Nitrobenzoyl chloride, similarly treated, gives 3·5 g. of *p*-nitrobenzoylhydrazide, m. p. 217°, sparingly soluble in boiling water and crystallising from alcohol in minute, pale yellow needles. *Benzaldehyde-*p-*nitrobenzoylhydrazone* is almost insoluble in cold alcohol, and its formation in alcoholic solution is a delicate test for benzaldehyde: one drop of benzaldehyde added to a hot alcoholic solution of the hydrazide yields a copious precipitate of very faintly yellow

needles, m. p. 259° (Found : C, 62·9; H, 3·9. $C_{14}H_{11}O_3N_3$ requires C, 62·4; H, 4·1%).

NN'-*Di*-p-*nitrobenzoylhydrazine* (4·0 g.) crystallises from nitrobenzene in very pale yellow needles, m. p. 291° (Found : C, 50·4; H, 3·3%). It forms a very sparingly soluble scarlet salt.

The authors desire to thank Mr. H. B. Somerset, B.Sc., for assistance in the initial stages of this work.

UNIVERSITY OF MELBOURNE. [*Received, February 1st, 1929.*]

CXXXIX.—*Molecular Volumes at Absolute Zero. Part III. Zero Volumes, Parachors, and Molecular Diameters.*

By SAMUEL SUGDEN.

IN Parts I and II of this series (J., 1927, 1780, 1786) no reference was made to the work of Biltz in the same field (*Nachr. Ges. Wiss. Göttingen*, 1926, 45; *Annalen*, 1927, **453**, 259). The first of these communications appeared in a journal not readily accessible in this country, and the second, which deals with additive relations in organic compounds, was published only a few months before the author's work was submitted for publication.

In these papers, Biltz has extended to organic substances the studies of limiting molecular volumes in the liquid and the solid state on which he has been engaged for some years. His zero volumes are obtained from a variety of different sources, *viz.*, extrapolation of liquid densities, densities in the solid state, and limiting molecular volumes deduced from the *X*-ray analysis of crystals; the values obtained by these methods usually agree within a few units %. For compounds, Biltz finds an additive relationship of the form $V_0 = \Sigma (nv_0/m)$, in which V_0 is the zero volume of the compound, and v_0, the zero volume of any one constituent free element obtained directly from its density, etc., is multiplied by the appropriate coefficient n/m, where n and m are small whole numbers. In many cases $n/m = 1$, *e.g.*, for carbon and the halogens; for hydrogen $n/m = \frac{1}{2}$, *i.e.*, this element in its compounds is assigned half the molecular volume it is found to occupy in the elementary condition. Similarly, for carbonyl oxygen $n/m = 1$, and for hydroxylic oxygen $n/m = \frac{1}{2}$.

This method of treating zero volumes differs in many respects from that adopted by the author (*loc. cit.*). Nevertheless, the atomic and structural constants deduced by the two methods show a

fairly close agreement, as may be seen from the examples shown below.

	V_0 (Biltz).	V_0 (Sugden).		V_0 (Biltz).	V_0 (Sugden).
C	3·4	1·1	O (carbonyl)......	10·7	13·0
H	5·8	6·7	O (hydroxyl) ...	3·6	3·0
CH_2.........	*15·0*	*14·5*	O (ethers)	3·6	*5·0*
Cl	16·5	19·3	N (amines)	0·0	0·0
Br	19·5	22·1	Double bond ...	4·0	8·0
I	24·3	28·3	Triple bond	12·0	15·5

Furthermore, the zero volumes of compounds deduced from the densities of liquids or solids, or from crystal analysis, have been shown by Biltz to agree closely, and can be predicted with a fair degree of accuracy by using either series of constants.

It is therefore of interest to examine the relationship between zero volumes (and, in addition, parachors and critical volumes) and the actual dimensions of the molecules. The latter quantity is somewhat difficult to define with certainty, but probably the best measure of the diameter of a molecule is provided by the modern work on the viscosity of gases. The mathematical theory of Chapman (*Phil. Trans.*, 1916, *A*, **216**, 347) leads to the formula

$$\pi\sigma^2 = \frac{0{\cdot}491(1 + \varepsilon)m\bar{V}}{\sqrt{2}\eta(1 + C/T)} \quad . \quad . \quad . \quad . \qquad (1)$$

Here η is the viscosity of the gas at an absolute temperature T, m is the mass of the molecule, σ its diameter, and $\bar{V}$ its mean velocity (which varies as $\sqrt{T}$); ε is usually very small and can be neglected and C is Sutherland's constant. Provided that Sutherland's law (*Phil. Mag.*, 1893, **36**, 507) holds, this formula gives a value for σ which is independent of temperature.

It will be seen from the formula that η is inversely proportional to the cross-sectional area of the molecule, and it is undoubtedly better to follow the procedure of Rankine (*ibid.*, 1921, **42**, 601, 615) and discuss collision areas rather than molecular diameters. In the present problem, however, molecular volumes have to be compared with the viscosity data, so some hypothesis about the shape of the molecule has to be made. In Table I, the molecules are regarded as spheres and the diameters of these spheres are compared. For the inert gases this procedure is probably accurate, but some uncertainty is introduced into the values for more complex molecules.

The volume occupied by an assemblage of N closely packed spheres of diameter σ is $V = N\sigma^3/\sqrt{2}$, hence $\sigma = \sqrt[3]{\sqrt{2}V/N} = 1{\cdot}326 \times 10^{-8}\sqrt[3]{V}$ cm., if V is the volume (in c.c.) of 1 g.-mol. In the liquid state we may assume a random distribution of molecules, so that the value of σ obtained in this way gives the average distance between the centres of adjacent molecules. In Table I the column headed σ_1

gives the molecular diameter (in Ångström units) calculated from the gas viscosity by formula (1). The data for the last five substances are taken from Hertzfeld ("Handbuch der Physik," Springer, Berlin, 1926, **22**, 409); for the others the values of σ_η are calculated from the observations of Rankine (*loc. cit.*). The columns headed σ_0, σ_p, and σ_c give the mean distances between the molecules respectively at absolute zero, as calculated from the author's zero volumes, at unit surface tension, as calculated from the parachor, and at the critical temperature. The last three columns give the ratio of these mean distances to σ_η.

If the molecules of a supercooled liquid are in contact with one another at absolute zero, then σ_0/σ_η should be approximately unity. There are, however, many reasons for supposing that the field of force around a molecule, which at small distances produces attraction, changes to one giving a force of repulsion when two molecules approach each other very closely. When thermal agitation ceases at 0° Abs., the molecules are probably distributed at such distances that there is neither attraction nor repulsion between them. On the other hand, the value of σ_η gives the closest approach of two rapidly moving molecules in a gaseous collision; hence σ_0/σ_η would be expected to be rather greater than unity. It will be seen that most of the substances give a value for this ratio of 1·2—1·3. Hydrogen and helium give much higher values, but this is only to be expected since the van der Waals attractive force for these

TABLE I.

Substance.	V_0.	[P].	V_c.	σ_η.	σ_0.	σ_p.	σ_c.	σ_0/σ_η.	σ_p/σ_η.	σ_c/σ_η.
He	22·3	20·2	57·6	1·94	3·73	3·61	5·12	1·92	1·86	2·64
Ne	12·8	25·1	41·8	2·32	3·10	3·88	4·60	1·34	1·67	1·98
A	22·4	53·8	75·2	2·90	3·74	5·01	5·73	1·29	1·73	1·97
Xe	33·0	—	112·7	3·44	4·25	—	6·41	1·24	—	1·86
H_2	22·0	35·1	46·9	2·18	3·72	4·34	4·78	1·71	1·99	2·19
Cl_2	38·6	111·5	123·7	4·12	4·48	6·38	6·61	1·09	1·55	1·60
Br_2	44·2	132·1	135·7	4·04	4·69	6·75	6·81	1·16	1·67	1·69
HCl	26·0	67·8	89·5	2·93	3·93	5·41	5·93	1·34	1·85	2·02
HBr ...	28·8	85·4	—	3·12	4·07	5·84	—	1·30	1·87	—
HI	35·0	105·3	—	3·43	4·34	6·26	—	1·26	1·83	—
NH_3 ...	19·1	63·8	71·9	2·85	3·63	5·30	5·51	1·27	1·86	1·95
C_2H_4 ...	37·4	99·5	—	3·71	4·43	6·14	—	1·20	1·66	—
C_6H_6 ...	70·9	206·3	256·1	4·20	5·49	7·84	8·42	1·31	1·87	2·01
Ethyl acetate	76·1	217·5	286·3	4·37	5·62	7·08	8·74	1·29	1·83	2·00
iso-Pentane	86·1	229·2	307·0	4·87	5·86	8·12	8·95	1·20	1·67	1·84
Propyl acetate	91·3	256·0	345·3	4·67	7·52	8·42	9·31	1·28	1·80	1·99
							Mean	1·32	1·78	1·98

gases is small. This is shown by many of their properties, *e.g.*, their low boiling points and critical temperatures; they also show a marked deviation from Sutherland's law at lower temperatures.

When the ratio σ_p/σ_η is considered, it will be seen that hydrogen falls into line with the other substances. The values oscillate about a mean of 1·78; the deviations may be ascribed chiefly to the omission of a correction for the shape of the molecule, but in some cases, notably with chlorine, may be due to uncertainties in the viscosity data. It is evident that, by comparing molecular volumes at equal surface tensions, the effect of the intermolecular field is largely eliminated, and a closer parallelism with the dimensions of molecules calculated from gas viscosities is obtained.

The ratio σ_c/σ_η calculated from the critical volume again shows high values for hydrogen and helium. For the remaining substances, the mean distance between the centres of adjacent molecules is about twice their diameter, *i.e.*, the " edges " of such molecules are separated by about one diameter. For liquids at the ordinary temperature the molecules will approach one another still more closely and cannot therefore be treated as point centres of force. It is this fact which is the chief difficulty in the way of an adequate theory of capillarity.

In general, it is to be expected that zero volumes and critical volumes will not be capable of accurate analysis as an additive function, but will show deviations for those substances of which the molecules have peculiar intermolecular fields. On the other hand, parachors, in which the influence of this field is largely eliminated, should approach more closely to the requirements of an ideal additive function. As an extreme example, the constants found for elementary hydrogen and for hydrogen in organic compounds may be quoted—the zero volumes show a large difference but the parachors are nearly identical :

	V_0.	[P].
H_2 (element)	22·0	35·1
2H (combined)	13·4	34·2

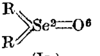
BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, March 20th*, 1929.]

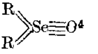
CXL.—*The Parachor and Chemical Constitution. Part XI. Arsenic and Selenium Compounds.*

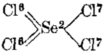
By WILLIAM JAMES REGINALD HENLEY and SAMUEL SUGDEN.

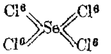
THE parachors of selenium compounds are of special interest in connexion with the question of the general validity of the octet rule. From the close chemical analogy with sulphur it would be expected that selenium in the selenoxides (I*a*) and the higher halides (II*a*), in which it exhibits valencies higher than two, would develop these

valencies by means of semipolar double bonds or singlet linkages, thus preserving a shell of eight electrons around the selenium atom. On the other hand, it has been suggested that the rule of eight


(Ia.)


(Ib.)


(IIa.)


(IIb.)

applies only to elements of low atomic number and that heavier elements can build up a larger external electronic shell. If this were true, it would permit of the existence of non-polar double bonds in the selenoxides (Ib) and of duplet linkages with the halogen atoms as in (IIb). The recent work of Gaythwaite, Kenyon, and Phillips (J., 1928, 2280, 2287) and of Edwards, Gaythwaite, Kenyon, and Phillips (*ibid.*, p. 2293), has revealed a number of characteristic differences between the behaviour of compounds of quadrivalent selenium and sulphur. Thus, quadrivalent sulphur is readily oxidised to the sexavalent state (*e.g.*, sulphoxides to sulphones), but the corresponding selenoxides cannot be oxidised to selenones. Further, selenoxides of the type $R_1R_2Se \rightarrow O$ have so far resisted all attempts at resolution, whereas the corresponding sulphur compounds are easily separated into their enantiomorphic forms. It seemed possible, therefore, that the octet rule might not hold for selenium, and if this were not the case the parachors of suitable compounds of this element should reveal the presence of the larger external electronic shell. It may be stated at once that the results of the investigation described below strongly support the application of the octet rule to selenium compounds and are opposed to any interpretation of the differences between sulphur and selenium compounds, which is based upon the presence of a group of more than eight electrons around the selenium atom.

Atomic Parachors of Selenium and Arsenic.—The first step in this investigation was the determination of the atomic constant for selenium. For this purpose only bivalent selenium compounds may be used, since in such substances there is no question as to the electronic structure of the linkages present in the molecule. This part of the work was facilitated by the loan of suitable substances by Dr. J. Kenyon (substances 1, 2, 3, 10, and 11) and Dr. Challenger (substances 4 and 5), to whom the authors tender their thanks. The parachors of these substances are collected in Table I, and give an atomic constant of 62·5 for selenium. Further evidence for this value is given by the parachors of selenophen (Briscoe and Peel, J., 1928, 1741), from which Se = 68·0, and of carbon sulphido-selenide (Briscoe, Peel, and Robinson, this vol., p. 56), from which Se = 58·7. This value is also supported by that of the neighbouring

TABLE I.

Atomic Parachor of Selenium.

No.	Substance.	Formula.	[*P*] obs.	Σ[*P*].	Se.
1	Diphenyl selenide	$SePh_2$	445·6	380·0	65·6
2	Diphenyl diselenide	SePh·SePh	506·5	380·0	63·2 × 2
3	Phenyl selenium bromide	SePhBr	321·4	258·0	63·4
4	*p*-Bromophenyl selenocyanate	$C_6H_4Br{\cdot}SeCN$	366·1	304·6	61·5
5	*p*-Chlorophenyl selenocyanate	$C_6H_4Cl{\cdot}SeCN$	349·3	201·1	58·2
				Mean	62·5

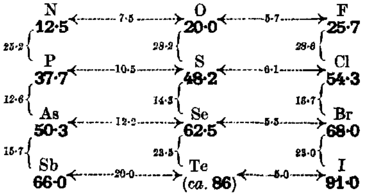
elements arsenic and bromine. For arsenic, measurements by Jaeger on the trichloride and tribromide were available, and to these we were able to add two chloroarsines of which specimens were kindly supplied by Dr. Johnson. The data for these compounds (Table II) give a mean parachor for arsenic of 50·3. These constants together

TABLE II.

Atomic Parachor of Arsenic.

No.	Substance.	Formula.	[*P*] obs.	Σ[*P*].	As.
6	Arsenic trichloride	$AsCl_3$	212·0	162·9	49·1
7	Arsenic tribromide	$AsBr_3$	253·5	204·0	49·5
8	Phenyldichloroarsine	$C_6H_5{\cdot}AsCl_2$	348·3	298·6	49·7
9	Diphenylchloroarsine	$(C_6H_5)_2AsCl$	487·1	434·3	52·8
				Mean	50·3

with those determined in earlier papers of this series show a regular variation of atomic parachor with atomic number. The vertical and the horizontal differences between the constants for adjacent atoms show a regular distribution and indicate that the constant for tellurium should be in the neighbourhood of 86 units.



Higher Valencies in Selenium Compounds.—The higher-valent compounds of selenium are conveniently divided into two classes for the purpose of discussing the type of valency linkage which they contain. The first group includes substances in which the valency is raised above the normal value of 2 by combination with a bivalent element, *e.g.*, oxygen in the selenoxides. If the octet rule

applies to selenium, then compounds of this group will contain a semipolar double bond (Formula I*a*). In the second group the additional valencies are used to hold univalent atoms, *e.g.*, chlorine in selenium tetrachloride, and here the octet rule requires the use of singlet linkages (Formula II*b*).

TABLE III.

Semipolar Double Bonds in Selenium Compounds.

No.	Substance.	Formula.	[*P*] obs.	Semi-polar.	Non-polar.
10	Diphenyl selenoxide	$Ph_2Se\overset{\rightharpoonup}{=}O$	461·6	460·9	485·7
11	Phenylseleninic acid ...	$\genfrac{}{}{0pt}{}{Ph}{HO}{>}Se\overset{\rightharpoonup}{=}O$	299·5	308·0	332·8
12	Selenium oxychloride ...	$Cl_2Se\overset{\rightharpoonup}{=}O$	181·1	189·5	214·3

Data for three compounds of the first group are in Table III. The parachors found for these substances indicate clearly that the double bond is semipolar. For diphenyl selenoxide the observed and the calculated parachors are in good agreement, but the other two substances give parachors even lower than that predicted for a semipolar double bond. In both cases this appears to be due to association.

The typical associated liquids, *viz.*, the lower alcohols and fatty acids, give parachors 4—8 units lower than the calculated (Sugden, J., 1924, **125**, 1189; Jones, J., 1928, 1196; Hunter and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 161). Since phenylseleninic acid contains a hydroxyl group, it should behave similarly, and the low value of its parachor can thus be accounted for.

The anomaly with selenium oxychloride requires a closer scrutiny, for the corresponding sulphur compound, thionyl chloride, gives a normal parachor ([P] obs. 174·5, [P] calc. 175·2; Sugden, Reed, and Wilkins, J., 1925, **127**, 1526). Two specimens of selenium oxychloride were examined, one, a commercial product purified by repeated distillation and fractional freezing and melting at 8°, and the second, a larger specimen, prepared from elementary selenium and repeatedly frozen until of constant melting point, 10° (corr.). Both gave the same value for the parachor; hence the anomaly found cannot be due to the presence of impurities.

The molecular weight of this substance in benzene was then investigated.* Over a range of concentration of 2—20 g. per 100 g. of benzene, the values found ranged from 166·5 to 195·7 ($SeOCl_2$ = 166·1). There is clearly a marked tendency for this substance to associate in benzene solution, and a still higher degree of association may be expected in the pure liquid. Further evidence for classify-

* Thionyl chloride gives a low molecular weight (109 instead of 119) by the cryoscopic method in benzene (Oddo and Sena, *Gazzetta*, 1899, **29**, ii, 318).

ing selenium oxychloride as an associated liquid is furnished by its low Ramsay–Shields coefficient $d\gamma(Mv)^{\frac{2}{3}}/dt = -1\cdot33$, its high dielectric constant (46·2 at 20°; Wildish, *J. Amer. Chem. Soc.*, 1920, **42**, 2607), and its remarkable solvent power.

The monohydrate of selenium oxychloride has also been examined. This substance, described by Lenher (*J. Amer. Chem. Soc.*, 1920, **42**, 2498), may be prepared either by adding water to the oxychloride or by the action of hydrogen chloride on selenium dioxide. The latter reaction has recently been studied by Robinson and Parker (J., 1928, 2853), who found that the compound could be distilled, but with some decomposition. From these methods of formation it probably has the structure $Se(OH)_2Cl_2$, and hence, if the octet rule holds, *it should contain two singlet linkages* (compare II*a*). The parachor found agrees with this hypothesis: $[P]$ obs. = 222·8, $[P]$ calc. (singlet formula) = 222·1. It is not possible without further evidence to determine whether the hydroxyl groups or the chlorine atoms are held by singlet links; since in phosphorus and antimony pentachlorides chlorine atoms linked by singlets appear to be moderately stable (Sugden, *loc. cit.*), the latter hypothesis seems the more probable.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 158; 1924, **125**, 27), and densities by means of the U-shaped pyknometer described in J., 1924, **125**, 1171. The tables below are set out in the same manner as in earlier papers of this series; the parachors are calculated by the formula $[P] = M\gamma^{\frac{1}{4}}/(D-d)$ where M = molecular weight, γ = surface tension (dynes/cm.), and D and d are the densities of liquid and vapour, respectively, d being neglected for the substances studied.

Arsenic trichloride and tribromide. The following data are due to Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1):

Arsenic trichloride (M = 181·3).				Arsenic tribromide (M = 314·7).			
t.	γ.	D.	$[P]$.	t.	γ.	D.	$[P]$.
−21·0°	43·8	2·245	207·7	49·6°	49·6	3·328	251·0
0·0	41·4	2·205	208·5	74·5	46·6	3·261	252·2
20·6	39·4	2·165	209·8	90·0	44·8	3·234	251·7
35·3	38·0	2·136	210·7	105·5	43·0	3·184	253·1
50·2	36·6	2·105	211·9	121·0	41·0	3·143	253·4
64·8	35·1	2·073	212·9	135·0	39·6	3·111	253·8
75·7	34·2	2·051	213·7	149·6	38·2	3·076	254·4
90·0	32·8	2·016	215·2	165·0	37·0	3·041	255·2
110·0	31·0	1·968	217·8	179·7	36·1	3·008	256·5
		Mean	212·0			Mean	253·5

Phenyldichloroarsine, $C_6H_5\cdot AsCl_2$, M = 223·0, b. p. 115°/9 mm. Densities determined: $D^{17\cdot6°}_{4°}$ 1·655; $D^{[illegible]}_{4°}$ 1·628; $D^{[illegible]}_{4°}$ 1·601; $D^{[illegible]}_{4°}$ 1·578; whence $D^{t°}_{4°} = 1\cdot677 - 0\cdot00125t$.

t	18·5°	42·0°	62·6°	79·0°
γ	44·64	41·51	38·72	37·33
D	1·654	1·624	1·600	1·578
$[P]$	348·3	348·3	347·5	349·1
				Mean 348·3

Diphenylchloroarsine, $(C_6H_5)_2AsCl$, M = 264·5, b. p. 172°/7 mm. Densities determined: $D_{4°}^{16·0°}$ 1·482; $D_{4°}^{42·0°}$ 1·387; $D_{4°}^{62·5°}$ 1·368; $D_{4°}^{80·5°}$ 1·350; whence $D_{4°}^{t°}$ = 1·427 — 0·000955t.

t	17·9°	42·5°	61·0°	80·5°
γ	45·30	42·65	40·37	38·32
D	1·411	1·386	1·369	1·350
$[P]$	486·3	487·6	487·0	487·5
				Mean 487·1

Diphenyl selenide, $(C_6H_5)_2Se$, M = 233·3, b. p. 168—170°/17 mm. Densities determined: $D_{4°}^{15·5°}$ 1·359; $D_{4°}^{43·5°}$ 1·332; $D_{4°}^{59·5°}$ 1·316; $D_{4°}^{77·5°}$ 1·298; whence $D_{4°}^{t°}$ = 1·374 — 0·00098t.

t	16·5°	39·5°	60·5°	79·5°
γ	44·81	42·26	39·41	37·84
D	1·358	1·335	1·315	1·296
$[P]$	444·7	445·7	444·6	446·7
				Mean 445·6

Diphenyl diselenide, $(C_6H_5)_2Se_2$, M = 312·5, m. p. 63°. Densities determined: $D_{4°}^{79·5°}$ 1·557; $D_{4°}^{115·0°}$ 1·518; $D_{4°}^{153·5°}$ 1·477; whence $D_{4°}^{t°}$ 1·644 — 0·00109t.

t	77·0°	97·5°	119·1°	139·2°
γ	40·02	38·49	36·64	34·32
D	1·556	1·538	1·514	1·492
$[P]$	505·2	506·1	507·9	507·0
				Mean 506·5

Phenyl selenium bromide, $C_6H_5·SeBr$, M = 236·2, m. p. 61°. Densities determined: $D_{4°}^{65·5°}$ 1·898; $D_{4°}^{77·5°}$ 1·875; $D_{4°}^{87·5°}$ 1·861; $D_{4°}^{97·5°}$ 1·845; whence $D_{4°}^{t°}$ = 2·001 — 0·0016t.

t	71·5°	80·5°	90·5°	103·0°
γ	43·18	41·55	40·29	38·39
D	1·876	1·862	1·850	1·836
$[P]$	322·7	322·0	320·6	320·2
				Mean 321·4

p-*Chlorophenyl selenocyanate*, $C_6H_4Cl·SeCN$, M = 216·7, m. p. 53·5—54·5°. Densities determined: $D_{4°}^{57·5°}$ 1·590; $D_{4°}^{68·5°}$ 1·579; $D_{4°}^{77·5°}$ 1·570; $D_{4°}^{89·0°}$ 1·557; whence $D_{4°}^{t°}$ = 1·650 — 0·00104t.

t	58·0°	65·5°	76·5°	85·5°
γ	43·02	42·20	41·12	40·03
D	1·590	1·582	1·570	1·561
$[P]$	349·0	349·3	349·5	349·2
				Mean 349·3

p-*Bromophenyl selenocyanate*, $C_6H_4Br{\cdot}SeCN$, $M = 261{\cdot}2$, m. p. 70·5—71·5°. Densities determined : $D_{4^\circ}^{75\cdot5^\circ}$ 1·842 ; $D_{4^\circ}^{80^\circ}$ 1·830 ; $D_{4^\circ}^{86\cdot0^\circ}$ 1·814 ; whence $D_{4^\circ}^{t^\circ} = 2{\cdot}042 - 0{\cdot}00264t$.

At 90° decomposition became perceptible, so the measurements were confined to lower temperatures.

t	76·0°	80·5°	85·5°	91·0°
γ	43·6	43·1	42·3	41·6
D	1·841	1·833	1·816	1·801
$[P]$	364·6	365·0	366·6	368·0
				Mean 366·1

Diphenyl selenoxide, $(C_6H_5)_2SeO$, $M = 249{\cdot}3$, m. p. 108°. Densities determined : $D_{4^\circ}^{116\cdot0^\circ}$ 1·382 ; $D_{4^\circ}^{136\cdot0^\circ}$ 1·375 ; $D_{4^\circ}^{137\cdot0^\circ}$ 1·364 ; $D_{4^\circ}^{147\cdot5^\circ}$ 1·335 ; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}487 - 0{\cdot}00089t$.

t	121·0°	133·0°	143·0°	151·5°
γ	42·32	41·07	40·21	39·31
D	1·379	1·368	1·359	1·351
$[P]$	461·0	461·4	462·0	462·2
				Mean 461·6

Phenylseleninic acid, $C_6H_5{\cdot}SeO_2H$, $M = 189{\cdot}2$, m. p. 122°. This substance decomposed rapidly a few degrees above its m. p., so one observation only was made at 123·0° (Found : $\gamma = 46{\cdot}7$; $D = 1{\cdot}652$; whence $[P] = 299{\cdot}5$).

Selenium oxychloride, $SeOCl_2$, $M = 166{\cdot}1$. This substance was prepared as described by Lenher (*loc. cit.*) and purified by distillation and repeated freezing. The specimen used had b. p. 181° (slight decomp.), and the m. p. (10°, corr.) was unchanged by four successive freezings in each of which half of the substance was removed as a "more fusible" fraction. Densities determined : $D_{4^\circ}^{16\cdot0^\circ}$ 2·445 ; $D_{4^\circ}^{38\cdot5^\circ}$ 2·398 ; $D_{4^\circ}^{59\cdot5^\circ}$ 2·356 ; $D_{4^\circ}^{77\cdot5^\circ}$ 2·314 ; whence $D_{4^\circ}^{t^\circ} = 2{\cdot}478 - 0{\cdot}00208t$.

t	17·0°	41·5°	62·5°	80·5°
γ	48·1	45·8	43·4	41·7
D	2·443	2·392	2·348	2·310
$[P]$	179·1	180·7	181·6	182·8

Another specimen, purchased from British Drug Houses and frozen out once, had m. p. 8° (corr.). Densities determined : $D_{4^\circ}^{14\cdot5^\circ}$ 2·443 ; $D_{4^\circ}^{40\cdot5^\circ}$ 2·390 ; $D_{4^\circ}^{54\cdot6^\circ}$ 2·359 ; $D_{4^\circ}^{72\cdot0^\circ}$ 2·322 ; whence $D_{4^\circ}^{t^\circ} = 2{\cdot}475 - 0{\cdot}00212t$.

t	15·0°	44·5°	60·5°	80·5°
γ	48·8	45·0	43·3	41·3
D	2·443	2·380	2·346	2·303
$[P]$	179·7	180·8	181·7	182·8

The Molecular Weight of Selenium Oxychloride.—The usual Beckmann apparatus was employed. The solvent used was A. R. benzene, dried with phosphorus pentoxide, and a little fresh pent-

oxide was added to the solution before each determination. Occasionally some difficulty was found in the formation of an ice-like solid form of benzene which gave a freezing point 0·2° too high; once the shower of small crystals had been obtained, it was easy to obtain readings to within $\pm 0{\cdot}002°$. To test the calibration of the thermometer, determinations were made with naphthalene and camphor as solutes at concentrations of about 4%. Found: naphthalene 127·4 (calc. 128), camphor 149·3 (calc. 152). The data found for selenium oxychloride ($M = 166{\cdot}1$) were:

Conc. (g./100 g.).	ΔT.	Molecular weight. R.	Molecular weight. B. & J.	Conc. (g./100 g.).	ΔT.	Molecular weight. R.	Molecular weight. B. & J.
1·925	0·578°	166·5	172·4	10·66	2·757°	193·0	193·6
4·713	1·345	175·3	179·3	14·61	3·75	194·3	191·6
6·06	1·641	184·6	188·1	19·83	4·95	195·7	189·3

The figures in the column headed R are calculated by Raoult's simple formula $M = KC/\Delta T$, in which the constant K is taken as 50. The last column gives the molecular weight from the equation of Bury and Jones (J., 1924, **125**, 2219; 1925, **127**, 1947), *viz.*, $M = 0{\cdot}78C(66{\cdot}95 - \Delta T)/\Delta T$. The latter expression gives a maximum in the molecular weight–concentration curve: this can scarcely be taken to have any physical significance but is a consequence of the mathematical form of the empirical equation. Both methods of calculation lead, however, to the conclusion that selenium oxychloride is appreciably associated in benzene solution at concentrations greater than 2% by weight, so the pure substance must be regarded as a highly associated liquid.

Selenium oxychloride monohydrate, $SeOCl_2,H_2O$, $M = 184{\cdot}1$, was prepared from selenium oxychloride (m. p. 8°) and water. Densities determined: $D_{4°}^{14\cdot8°}$ 2·253; $D_{4°}^{42\cdot3°}$ 2·202; $D_{4°}^{63\cdot5°}$ 2·160; $D_{4°}^{78\cdot6°}$ 2·134; whence $D_{4°}^{t°} = 2{\cdot}282 - 0{\cdot}00189t$.

t	16·2°	43·1°	61·45°	77·1°	94·4°
γ	52·48	49·62	46·73	45·78	43·70
D	2·251	2·200	2·165	2·136	2·103
$[P]$	220·1	222·1	222·5	224·2	225·1
				Mean	222·8

One of us (S. S.) is indebted to the Research Fund Committee of this Society for a grant which has partly defrayed the cost of this investigation.

Birkbeck College (University of London),
Fetter Lane, E.C. 4. [*Received, March 20th*, 1929.]

CXLI.—*The Thermal Decomposition of Methane. Part I. Decomposition in Silica Bulbs.*

By G. C. HOLLIDAY and H. C. EXELL.

THE static experiments upon the decomposition of methane described in this paper form part of an investigation of the secondary reactions of coal carbonisation in gas retorts which is proceeding in the laboratories of the Gas Light and Coke Co. At an early date it is hoped to publish the results obtained by the streaming method to which reference is made, and then to discuss the bearing of the work upon industrial practice in gas manufacture.

Although much attention is at present being paid to the synthesis of higher hydrocarbons (Fischer, *Brenn. Chem.*, 1928, **9**, 309; Wheeler and Wood, *Fuel*, 1928, **7**, 535) from methane, the literature gives very little information with regard to the rate of decomposition of the gas. With certain catalysts the reaction appears to be a straightforward unimolecular one (Schwab and Pietsch, *Z. physikal. Chem.*, 1926, **121**, 189), whereas on other surfaces the order is uncertain (Bone and Coward, J., 1908, **93**, 1197). Our experiments have been chiefly confined to surfaces of silica, coke, and retort graphite, and have shown that under these conditions the decomposition is by no means so simple as might be expected, for between 900° and 1200° the initial velocity of decomposition is very great but later becomes so strongly retarded that for all practical purposes a condition of false equilibrium, far removed from the theoretical, is set up.

EXPERIMENTAL.

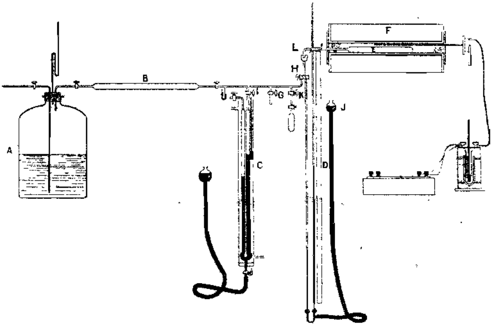
Fig. 1 shows the apparatus used. It consists of a reservoir for methane A, a phosphoric oxide drying tube B, a measuring burette C, a manometer D, and a clear silica bulb E, heated to the required temperature in the double-wound nichrome furnace F. The temperature of the bulb over its whole length could be kept constant within 1—2°.

To carry out a run, dry methane was first passed into C, the bulb evacuated *via* tap G, tap H closed, tap I opened, and the volume of methane in C read. Tap H was opened and methane allowed to enter the bulb. Tap H was then turned through 180° and the mercury raised by means of the reservoir J to the constant-volume mark L, above the ground joint. Readings could then be taken at intervals showing the increase of pressure resulting from the dissociation. A first reading could be obtained within a minute of the entry of gas into the bulb. The initial pressure P_0 was calculated from the amount of methane admitted and the volume of the bulb,

previously determined by calibration with nitrogen. Before the second reading in C was taken, the capillary in tap H was filled with mercury. At the end of the run a sample of the resulting gas could be taken *via* taps K and H.

Temperatures were accurately controlled by means of a platinum–platinum-rhodium thermocouple with its cold junction in ice. The capacity of the bulbs varied from 130 to 150 c.c. The results are corrected where necessary for hydrogen diffusion, which was, however, negligible at 900° and still very small at 1000° and 1100°, owing to the thickness of the silica used. Agreement between pressure measurements and gas analysis was usually within 1%.

FIG. 1.



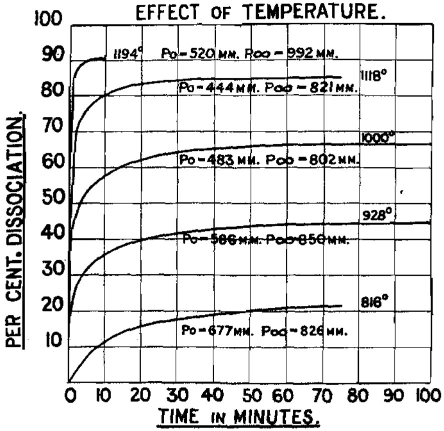
Bulbs were coated with methane carbon in all cases before the commencement of a series of runs.

Preparation of Methane.—In the early experiments methane was prepared from aluminium carbide. The crude gas was purified by passing it at a rate of 2 litres per hour successively through ammoniacal cuprous chloride, 50% sulphuric acid, 50 cms. of copper oxide contained in a tube heated to 270°, alkaline sodium hydrosulphite, and 50% potassium hydroxide. Gas of 99% purity, the remainder being chiefly nitrogen with a trace of hydrogen, can be prepared in this way. In the later experiments, cylinder methane supplied by Messrs. Insoles, Ltd., of Porth, was purified by fractionation in liquid air, and a gas of 99·9% purity obtained. Gas prepared in both ways gave precisely the same results.

Results.—Fig. 2 shows a few results obtained in a bulb of volume

129·6 c.c. and internal surface 194·8 sq. cm. It will be seen that in all cases there is a very rapid initial decomposition followed by extremely slow dissociation and that the percentages of methane remaining for *all* practical purposes stable after some 60 minutes are very much greater than we should expect from the true equilibrium values (see later). Two experiments at 900° show how slowly the methane is decomposing in the later stages. Beginning in each case with 660 mm., there remained after 113 minutes 41·9% and after 342 minutes 38·2% of methane, *i.e.*, less than 1% of methane

Fig. 2.



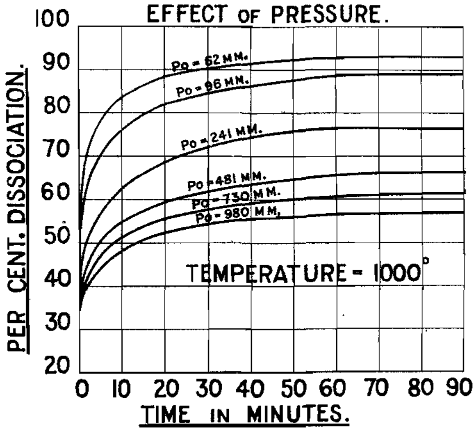
disappears per hour. Similarly at 1000° with an initial pressure of 540 mm. in each case, 1·5% of methane decomposed per hour in the later stages.

Effect of Pressure.—Some preliminary experiments at 900° showed that the lower the initial pressure the greater is the final amount of dissociation. A series of careful experiments at 1000° was then carried out and Fig. 3 shows the results obtained when the initial pressure varied from 60 to 980 mm. The curves again have the appearance of true dissociation equilibria, *i.e.*, higher dissociation at lower pressures.

Effect of Added Hydrogen.—Experiment showed that hydrogen

added initially behaves in the same way as that produced by dissociation, whether it is mixed initially with the methane or introduced previously into the bulb. If the initial mixture corresponds to some point on the first part of the curve, the rate is exactly the same as if dissociation of pure methane had already reached a point corresponding to the initial mixture. If more than the "equilibrium" amount of hydrogen is present initially the curve is practically a straight line and the methane decomposes extremely

FIG. 3.



slowly (Fig. 4). It will be noted, however, that no synthesis back to the "equilibrium" value occurs with excess of hydrogen.

Effect of Other Gases.—Nitrogen and carbon monoxide have no effect on the rate or on the final amount of dissociation if the initial partial pressure of methane is the same. At a constant total pressure, however, they act as diluents and, by reducing the partial pressure of methane, increase the percentage decomposition.

Discussion.

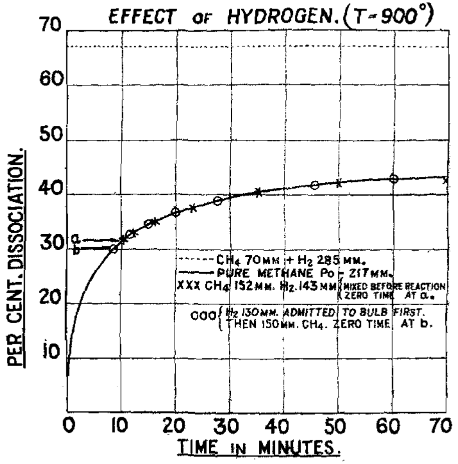
All the experimental results suggest a reaction approaching an equilibrium which, however, bears no relation to the true reversible equilibrium in the presence of special catalysts. Saunders's

equation (*J. Physical Chem.*, 1924, **28**, 1151) for the true equilibrium of methane and hydrogen in contact with graphite, *viz.*,

$$\log K_p = 4008/T - 1{\cdot}75 \log T + 0{\cdot}00063T - 0{\cdot}7,$$

agrees fairly well with the results obtained by Pring and Fairlie (J., 1912, **101**, 91). The true equilibrium amounts of methane, calculated from this equation for the temperatures and final pressures shown in Fig. 2, are given in Table I (E_{CH_4}, col. 3). The

FIG. 4.



actual amounts of methane, e_{CH_4}, remaining in the experiments a[re] shown in col. 4, and it will be seen that they are very much great[er] than the true equilibrium values.

TABLE I.

Temp.	Total pressure (mm.) after 60 mins.	E_{CH_4} (mm.).	e_{CH_4} (mm.).
816°	819·2	19·0	534·6
928	845·3	9·3	326·7
1000	799·3	5·6	166·7
1118	820·6	3·2	66·4
1194	(992) *	2·4	48·0

* After 10 minutes.

It is clear that the decomposition is not a simple unimolecular reaction, proceeding simply to the true final equilibrium point. The apparent equilibria are due possibly to two causes: (1) The solid deposited by methane may not be pure carbon but a high hydrocarbon with a greater vapour pressure than carbon, in which case the equilibrium concentrations of methane would be *higher* (compare equilibrium of carbon monoxide, carbon, and iron oxide with different forms of carbon; Schenk and Heller, *Ber.*, 1905, **38**, 2139). (2) The reaction is being very strongly retarded by selective adsorption.

Since synthesis from hydrogen and the solid deposited by previous decomposition of methane could not be effected to the extent required by the " equilibrium " value, and since the " equilibrium " values vary with the extent of the surface (unpublished results), the first explanation is not valid. The second, however, appears to be the true one. Hinshelwood (" Kinetics of Chemical Change in Gaseous Systems," p. 158; J., 1925, **127**, 1114) has given examples of retardation, and shows that the lower the initial pressure the greater the velocity of reaction (compare nitrous oxide and ammonia). Our experiments show that the retardation in the case of methane is extremely strong and is almost certainly due to the preferential adsorption of hydrogen, which finally protects the surface so efficiently that further decomposition of methane is practically prevented.

A glance at the velocity curves shows that at most of the temperatures used the greater part of the reaction is over before the first reading can be taken. Thus it is not yet possible to determine the order of the reaction or the complete velocity equation, which will probably involve hydrogen as a retarding factor to some power of its concentration. Experiments are in progress on the course of the rapid reaction at low pressures, and it is hoped that these will throw light on the present results.

Whatever the final form of the velocity equation, the similarity between the " equilibrium " values and true equilibria is remarkable. In fact, if the concentrations of hydrogen and methane remaining after one hour are regarded as true equilibrium values, the results shown in Fig. 3 give a fairly good constant for the expression $p_{CH_4}/p^2_{H_2} = C$, which means that the amount of initial decomposition on a given surface for any pressure of methane can be calculated from one result. If P_0 is the initial pressure of methane, and P_∞ the total pressure after 1 hour, then the values of C at a temperature of 1000° (Table II) are seen to be approximately constant over the range 60—980 mm. for P_0.

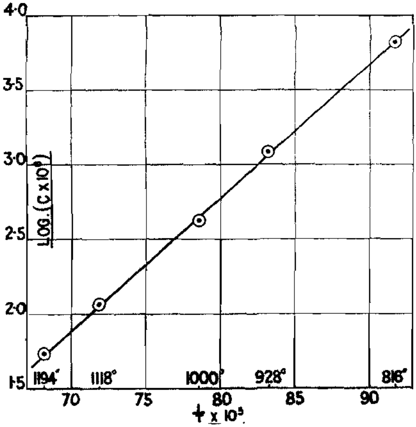
Further, if C is found for the results at different temperatures

TABLE II.

P_0 (mm.).	P_∞ (mm.).	p_{CH_4}.	p_{H_2}.	$C \times 10^7$.
62	119·4	4·6	114·8	3491
96	181·0	11·0	170·0	3807
241	425·6	56·4	369·2	4139
481	796·1	165·9	630·2	4179
730	1171·7	288·3	883·4	3694
980	1533·7	426·3	1107·4	3477

shown in Fig. 2 and log C is plotted against temperature, a straight line is obtained (Fig. 5), again showing close analogy with a true equilibrium reaction. For a given surface, therefore, the amount

FIG. 5.



of rapid dissociation of methane at any pressure and temperature *can be calculated from two results at different temperatures.* There is at present no theoretical justification for the constant C, but it is likely to be of practical use.

Ethane.—The following experiment shows that methane and hydrogen resulting from the decomposition of ethane exhibit the same retardation as methane itself, and give the correct C value for the temperature and pressure of the experiment. 297 M.m. of ethane containing 3·4% of nitrogen were admitted to a bulb of very nearly the same size as that used for methane. The temperature

was 929°. The decomposition initially was extremely rapid but practically stopped when the total pressure was 663 mm. Analysis of the residual gas gave 29·8% CH_4, 68·7% H_2, and 1·5% N_2. Assuming that the methane and hydrogen are in equilibrium, and calculating C from their partial pressures, we find that log ($C \times 10^6$) is 2·9807, which lies very close to the same value for methane at 929°, *viz.*, 3·05 (Fig. 5).

Experiments on Porcelain.—A porcelain bulb of approximately the same size as the silica bulbs was used for a few experiments at 1000°. In all cases the retardation was just as marked, and the "equilibrium" values almost exactly the same as those obtained on silica.

Experiment with a Nickel Catalyst.—One of the silica bulbs used in the previous runs was coated with nickel by decomposition of a solution of the nitrate and reduction in the bulb itself. At 900° the velocity of decomposition of the methane was enormously increased, no retardation taking place. Only 3% of methane remained after 18 minutes, showing that the true equilibrium point was being rapidly approached.

Effect of Surface.—Previous workers have assumed that at least up to 1300° the decomposition of methane is a purely surface reaction, but very little quantitative evidence is given. If a gas reaction and a surface reaction are occurring simultaneously, differentiation can usually be achieved by measuring velocities on surfaces of different areas, and the value of the velocity coefficient found by extrapolation to correspond to a zero value for the ratio surface : volume is the coefficient for the homogeneous reaction. An attempt was made to determine the influence of surface. A silica bulb packed with thin silica tubing and sealed into a larger silica bulb was used, the outer bulb serving as a jacket of hydrogen to prevent diffusion entirely. The results in this bulb, however, were disappointing, the analyses diverging considerably from the pressure readings. Experiments with pure hydrogen showed that the velocity of decomposition was being masked by rapid solution of hydrogen in the silica packing, the rate of which was of the same order as the decomposition itself and affected the pressure readings in the reverse direction by lowering the total pressure. The amount of hydrogen absorbed increases as the temperature is raised and is directly proportional to the total hydrogen pressure. At 900°, 6·4% of the pressure of hydrogen was absorbed by 105 g. of silica packing in a bulb in which the free space was 51·8 c.c.; at 1000°, 10·6%; and at 1100°, 16%, most of the absorption being complete in 10 minutes in all cases. It will be seen that such absorption would seriously affect the accuracy of velocity determinations carried out under the above conditions

and with the object specified; it was therefore necessary to use a streaming method to find the effect of surface, and the results obtained will be published shortly.

Summary.

(1) The decomposition of methane on silica at temperatures between 800° and 1200° has been studied.

(2) Retardation is so strong in all cases that for practical purposes a false equilibrium is obtained.

(3) Results obtained over a wide range of pressures show that values of $p_{CH_4}/p^2_{H_2}$ are constant, and the effect of temperature on the constant is exactly analogous to its effect on true equilibria.

(4) Similar results are obtained on porcelain.

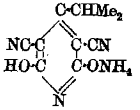
(5) Ethane decomposes to give the same " equilibrium " mixture of methane and hydrogen.

[*Received, February 9th*, 1929.]

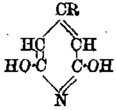
CXLII.—*The Constitution of Guareschi's Cyano-butadiene Acids. An Attempt to Synthesise β-*iso*Propylglutaconic Acid.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

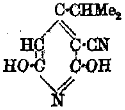
THE simplest method for preparing β-*iso*propylglutaconic acid (III), required for comparison with *cis*-homocaronic acid (J., 1928, 431), would appear to be the hydrolysis of the cyano-acid (II). According to Guareschi (*Mem. Accad. Sci. Torino*, 1907, **57**, 281) this cyano-acid is formed when the ammonium salt (I) is digested with sulphuric acid.



(I.)



(IV.)



(V.)

CN·CH:C(CHMe$_2$)·CH$_2$·CO$_2$H (II.)

HO$_2$C·CH:C(CHMe$_2$)·CH$_2$·CO$_2$H (III.)

On reviewing the properties of this cyano-acid and a number of related acids described by Guareschi, it appeared to us unlikely that these substances could have the constitution ascribed to them and that in all probability they were the isomeric dihydroxypyridines of the general formula (IV), *i.e.*, the imides of the glutaconic acids.

The properties more especially pointing to this constitution are (i) their high melting points, (ii) their sparing solubility in organic media, (iii) their colour reactions with ferric chloride and with potassium nitrite, and (iv) their tendency to develop a blue colour on keeping: all of these are properties which have been shown by Rogerson and Thorpe (J., 1905, 87, 1685) to be characteristic of the dihydroxypyridines.

On repeating the condensation of *iso*butaldehyde and ethyl cyanoacetate under the conditions used by Guareschi (*Atti R. Accad. Sci. Torino*, 1902, 38, 290) we had no difficulty in preparing the ammonium salt (I) in excellent yield. When this salt was hydrolysed with sulphuric acid (60%), and the solution cooled and diluted, a small quantity of a crystalline solid, m. p. 273°, separated which was evidently 2 : 6-*dihydroxy*-3-*cyano*-4-iso*propylpyridine* (V); on removal of the excess of mineral acid with ammonia a substance was obtained which had m. p. 213—214° and was undoubtedly 2 : 6-*dihydroxy*-4-iso*propylpyridine* (IV, R = $CHMe_2$) and not the isomeric acid (II). This was established by the preparation of the *hydrochloride*, the *di*-p-*nitrobenzoyl* derivative, and the *oxime*. We did not obtain a substance of m. p. 177—178°, which according to Guareschi is the m. p. of the cyano-acid. It is probable that Guareschi actually obtained a mixture of (IV) and (V), since in our preliminary experiments we isolated a low-melting substance which crystallised well but was shown by further experiments to be a mixture.

These experiments having shown that Guareschi's *iso*propylcyano-acid was a pyridine derivative, it appeared desirable to prepare the corresponding methylcyano-acid supposed to be formed by the hydrolysis of the condensation product from acetaldehyde and ethyl cyanoacetate (*Atti R. Accad. Sci. Torino*, 1900, 36, 414). The properties of the cyano-acid resembled very closely those of the 2 : 6-dihydroxy-4-methylpyridine prepared by Rogerson and Thorpe (*loc. cit.*, p. 1689). Repetition of Guareschi's experiments has shown, as was anticipated, the product of the hydrolysis of the ammonium salt to be the dihydroxypyridine. This was characterised by the preparation of the oxime, m. p. 174°, and the dibenzoyl derivative, m. p. 94°. In agreement with Rogerson and Thorpe it has been found that both the hydrated and the anhydrous form of the dihydroxypyridine melt at the same temperature, 193—194°, and not at 199—200° and 225—227°, respectively, as observed by Guareschi.

It is to be concluded that the various cyano-acids described by Guareschi are in reality dihydroxypyridines, and confirmatory evidence of this is afforded by the melting points of the dimethyl-

and methylethyl-dihydroxypyridines and of the isomeric cyano-acids prepared by Rogerson and Thorpe (m. p. 175° and 189°) and by Guareschi (m. p. 175—176° and 191·5—192°) respectively.

In an attempt to prepare the glutaconic acid by the removal of hydrogen bromide from *ethyl α-bromo-β-isopropylglutarate* (VI) by diethylaniline, the main product of the reaction was the *lactonic ester* (VII), no trace of either an unsaturated or a cyclic ester being

(VI.) $EtO_2C\cdot CHBr\cdot CH(CHMe_2)\cdot CH_2\cdot CO_2Et$

(VII.) $EtO_2C\cdot CH\cdot CH(CHMe_2)\cdot CH_2\cdot CO$
$\qquad\quad$ └───────O───────┘

apparently formed. This ester has not been described previously, although the lævorotatory form of the lactonic acid was obtained by Semmler (*Ber.*, 1903, **36**, 1749) by the oxidation of phellandrene. The constitution of the synthetic lactone (VII) was established by its oxidation to *iso*propylsuccinic acid. In addition to the lactonic ester, a quantity of an ester with a much lower boiling point was formed by the action of diethylaniline on the bromo-ester. This was found to be ethyl *iso*propylglutarate, simple replacement of the bromine by hydrogen having occurred. Although this reaction is remarkable, it is not without analogy, since Haerdi and Thorpe (J., 1925, **127**, 1242) found that when ethyl α-bromo-β-phenylglutarate was digested with pyridine a similar reaction took place with formation of ethyl β-phenylglutarate. The mechanism of this reaction is not clear, but during the treatment of the bromo-ester with diethylaniline the formation of a volatile oil, probably ethyl bromide, was observed.

It was hoped to prepare ethyl β-hydroxy-β-*iso*propylglutarate (i) by treatment of ethyl acetonedicarboxylate with the appropriate Grignard reagent or (ii) by the condensation of ethyl *iso*butyrylacetate (Bouveault and Bougert, *Bull. Soc. chim.*, 1902, **27**, 1038) with ethyl bromoacetate in the presence of zinc. In both cases, however, the keto-group reacted in its enolic form, so rendering the experiments nugatory. It is possible that the required glutaconic acid could be prepared in poor yield by the method of Rogerson and Thorpe (*loc. cit.*) from ethyl *iso*butyrylacetate and ethyl cyanoacetate, but since the keto-ester can only be prepared with difficulty we have not investigated this reaction.

E X P E R I M E N T A L.

Ammonium Salt of 2 : 6-Dihydroxy-3 : 5-dicyano-4-methylpyridine and 2 : 6-Dihydroxy-4-methylpyridine.—The ammonium salt was prepared by Guareschi's method (*Atti R. Accad. Sci. Torino*, 1900, **35**, 454); it crystallised from water in glistening thin prisms

(Found: N, 29·4. Calc.: N, 29·2%). The dihydroxypyridine was obtained when the ammonium salt was hydrolysed with sulphuric acid (60%), and separated from the aqueous solution after removal of the excess of mineral acid with ammonia. It crystallised from hot water, in which it was somewhat readily soluble, in small glistening prisms, m. p. 193—194°, containing one molecule of water of crystallisation, which was lost at 110° without alteration of the melting point. It was not found possible to raise the m. p. to 199—200° as found by Guareschi, but in other respects our substance resembled in all particulars the cyano-acid described by him. It reacted as a monobasic acid, gave with ferric chloride a violet coloration, reduced an ammoniacal silver solution, and in alkaline solution became blue on exposure to the air (Found: H_2O, 12·9; N, 11·3; *M*, 125·7. Calc.: H_2O, 12·6; N, 11·2%; *M*, 125). Rogerson and Thorpe found that 2 : 6-dihydroxy-4-methylpyridine had similar properties, and the identity of the two substances was confirmed by the preparation of the oxime, small yellow prisms, decomp. 174—175° (R. and T. give 178°), and the dibenzoyl derivative, m. p. 94°.

Ammonium Salt of 2 : 6-*Dihydroxy*-3 : 5-*dicyano*-4-iso*propylpyridine and* 2 : 6-*Dihydroxy*-4-iso*propylpyridine*.—The ammonium salt, prepared as described by Guareschi (*Atti R. Accad. Sci. Torino*, 1902, **38**, 290), crystallised from hot water, in which it was sparingly soluble, in glistening prisms which did not melt below 295° (Found: N, 25·2. Calc.: N, 25·5%).

Preliminary experiments having shown that on hydrolysis with sulphuric acid (60%) a mixture of products was formed, the following conditions were found most convenient for their separation. A mixture of the ammonium salt (5 g.) and sulphuric acid (60% by weight; 90 c.c.) was boiled under reflux until all evolution of carbon dioxide had ceased (1·5 hours). The cooled product was mixed with water (25 c.c.), and ammonia added until a precipitate just began to form. After remaining in the ice-chest for some hours, the solid, *A* (0·25 g.), was collected, and the filtrate treated with ammonia until it was faintly acid to Congo-red. A voluminous precipitate, *B* (2·8 g.), separated and was collected. The filtrate was evaporated to dryness on the water-bath and the residual salts were extracted with alcohol, which on evaporation gave a third fraction, *C* (0·5 g.).

Fraction *A*, m. p. about 248°, crystallised from water in long glistening needles. 2 : 6-*Dihydroxy*-3-*cyano*-4-iso*propylpyridine* was found to be very sparingly soluble in water, readily soluble in alcohol, but insoluble in the ordinary organic media. From water it crystallised with one molecule of water of crystallisation, which it

lost at 110° and then had m. p. 273°. With ferric chloride in aqueous solution it gave a deep purple coloration which became cherry-red on warming. It reduced an ammoniacal silver solution on warming and was readily soluble in alkalis, behaving on titration as a monobasic acid. On keeping, alkaline solutions of the hydroxy-pyridine developed a purple colour (Found: H_2O, 9·4; N, 16·0; *M*, 180·3. $C_9H_{10}O_2N_2,H_2O$ requires H_2O, 9·2%. $C_9H_{10}O_2N_2$ requires N, 15·7%; *M*, 178).

Fraction *B*, m. p. 211°, crystallised from water, in which it was very sparingly soluble, in soft needles, m. p. 213—214°. 2 : 6-*Dihydroxy*-3-iso*propylpyridine* is very sparingly soluble in all the ordinary organic solvents with the exception of methyl and ethyl alcohols. With ferric chloride its aqueous solution gives a purple coloration which disappears on warming. It reduces an ammoniacal silver solution and behaves on titration as a monobasic acid, the alkaline solution becoming purple on keeping (Found: N, 9·0; *M*, 153·5. $C_8H_{11}O_2N$ requires N, 9·2%; *M*, 153). The *hydrochloride* crystallised from concentrated hydrochloric acid in glistening plates (Found: HCl, 18·9. $C_8H_{11}O_2N,HCl$ requires HCl, 19·3%). The benzoyl derivative was a gum, but the *di*-p-*nitrobenzoyl derivative* crystallised from acetic acid in glistening slender needles, m. p. 200—201° (Found: N, 9·5. $C_{22}H_{17}O_8N_3$ requires N, 9·3%). The *oxime* was slowly deposited when an alkaline solution of the pyridine containing an excess of sodium nitrite was treated with acetic acid. It crystallised from alcohol in pale yellow leaflets, m. p. 123—124° (Found: N, 15·2. $C_8H_{10}O_3N_2$ requires N, 15·4%). It dissolved in sodium carbonate, yielding a magenta-red solution.

Fraction *C* melted indefinitely at about 190°. On digestion with a large volume of acetone a very sparingly soluble portion remained undissolved; this crystallised from water in needles, m. p. 265—270°, and was identified as the dihydroxycyanopyridine. The portion soluble in acetone gave after repeated crystallisation from water a further small quantity of the dihydroxypyridine.

Bromination of β-isoPropylglutaryl Chloride. Ethyl α-Bromo-β-isopropylglutarate.—β-*iso*Propylglutaric acid (30 g.) was mixed with phosphorus pentachloride (37 g.) and after the formation of the acid chloride was complete, dry bromine (28·6 g.) was gradually added, the mixture being gently warmed on the water-bath. Absorption of the bromine was complete in 4 hours. The acid chloride was poured into well-cooled alcohol and the next day ice was added. The heavy oil thus precipitated was dissolved in ether, and the ethereal solution well washed with sodium carbonate solution, dried, and evaporated. On fractionation under 28 mm., practically the whole of the residue distilled at 170—180° with

slight decomposition (yield, 41 g.). For analysis the *bromo-ester* was redistilled, b. p. 178°/30 mm. (Found : Br, 22·9. $C_{12}H_{21}O_4Br$ requires Br, 25·9%).

Action of Diethylaniline on Ethyl α-Bromo-β-isopropylglutarate.—The bromo-ester (40 g.) was mixed with freshly distilled diethylaniline (60 g.) and heated at 190—200° for 8 hours. The cooled solution was poured into an excess of dilute hydrochloric acid (1 : 1), the ester extracted with ether, and the ethereal extract well washed with dilute hydrochloric acid to remove diethylaniline, dried and evaporated. On fractionation under 20 mm., the residual oil was readily separated into two main fractions, (*a*) b. p. 150—160° (10 g.) and (*b*) b. p. 165—180° (12 g.). On redistillation, (*a*) boiled very constantly at 154—155°/21 mm., and (*b*) boiled mainly at 170—180°/25 mm. In a second experiment using 52 g. of the bromo-ester from a different preparation an identical result was obtained, the two fractions being respectively 14 and 16 g.

Fraction (*a*), which contained a trace of bromine and therefore was not analysed, was hydrolysed with methyl-alcoholic potassium hydroxide solution; the acid, isolated by means of ether in the usual manner, crystallised almost completely on removal of the solvent. It was purified through the sparingly soluble calcium salt, and after crystallisation from benzene it had m. p. 101—102°. It was identified as β-*iso*propylglutaric acid by the method of mixed m. p., by analysis (Found: C, 55·5; H, 8·1. Calc.: C, 55·1; H, 8·0%), and by the preparation of the semianilide, m. p. 121°. It was observed, contrary to the statement in Beilstein's "Organische Chemie" (II, 703), that the acid is somewhat sparingly soluble in cold benzene but readily soluble in chloroform.

The filtrate from the sparingly soluble calcium salt yielded a small quantity of a liquid acid, which was added to fraction (*b*). Fraction (*b*) was hydrolysed with methyl-alcoholic potassium hydroxide solution, a sparingly soluble potassium salt separating. The acid, isolated by ether, was an oil which showed no tendency to crystallise. On treatment with acetyl chloride a small quantity of an anhydride was formed, which was separated by means of sodium bicarbonate solution and identified as β-*iso*propylglutaric anhydride. The liquid acid, recovered from the sodium bicarbonate solution, was esterified with alcohol and sulphuric acid in the usual manner. The resulting ester had b. p. 178°/26 mm., $n_D^{20°}$ 1·4466, and analysis showed it to be the *ethyl* ester of the *lactone* of dl-α-*hydroxy*-β-*isopropylglutaric acid* (Found: C, 60·3; H, 8·4. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

The *lactonic acid* obtained from the ester by hydrolysis was a colourless viscid oil and showed no tendency to crystallise. It was

extremely readily soluble in all the ordinary organic solvents with the exception of light petroleum and gave a sparingly soluble copper salt on treatment of its aqueous solution with copper acetate. Its composition was confirmed by titration (Found : *M*, 171·1, 189. $C_8H_{12}O_4$ requires *M*, 172. $C_8H_{14}O_5$ requires *M*, 190). The lactonic acid, which was only slowly attacked by potassium permanganate in alkaline solution, was oxidised by lead peroxide in the presence of sulphuric acid, *dl-iso*propylsuccinic acid being formed. This had m. p. 115—116° after crystallisation from benzene, and the m. p. was not depressed by admixture with an authentic specimen of this acid for which we are indebted to Dr. Henry.

We are grateful to Dr. J. D. A. Johnson for his valuable assistance in connexion with the analytical portion of this work and we desire to express our indebtedness to the Government Grant Committee of the Royal Society for a grant which has covered most of the expenses of this investigation.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E. 1. [*Received, March 7th,* 1929.]

CXLIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part VIII. The Bromination of* 10-*Chloro*-5 : 10-*dihydrophenarsazine and Some of its Derivatives.*

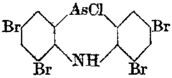
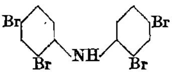
By LESLIE ALDERMAN ELSON, CHARLES STANLEY GIBSON, and JOHN DOBNEY ANDREW JOHNSON.

2 : 10-DICHLORO-, 1 (or 3) : 10-dichloro-, and 2 : 8 : 10-trichloro-5 : 10-dihydrophenarsazines have been prepared by the condensation of the appropriate halogenated diphenylamine and arsenious chloride in *o*-dichlorobenzene solution (J., 1926, 2246). An attempt to prepare 2 : 4 : 6 : 8 : 10-pentachloro-5 : 10-dihydrophenarsazine by condensing arsenious chloride with 2 : 4 : 2′ : 4′ : tetrachlorodiphenylamine was, however, unsuccessful (*loc. cit.*, p. 2243, footnote). Three explanations of the latter observation may be advanced, *viz.*, (*a*) that the formation of the additive compound of the substituted diphenylamine and arsenious chloride which has been assumed to precede the formation of the phenarsazine derivative (J., 1926, 454; 1928, 2208) might be inhibited if the basicity of the :NH group were diminished by negative substituents in the diphenylamine nucleus, (*b*) the steric effect of the *oo*′-chlorine atoms might prevent the formation of this additive compound, and (*c*) the pentachloro-5 : 10-di-

hydrophenarsazine might be too unstable to exist. The fact that *o*-, *m*-, and *p*-nitrodiphenylamines do not condense with arsenious chloride (*loc. cit.*, footnote) seems to support (*a*), but, on the other hand, the more basic *o*-aminodiphenylamine also does not condense with arsenious chloride. That the steric effect mentioned in (*b*) can have little effect on this reaction would appear to be proved by the facts that phenyl-α-naphthylamine (Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218) and di-α-naphthylamine (J., 1926, 463) condense readily with arsenious chloride.

In order to test the third explanation it seemed desirable to ascertain whether halogenated derivatives of 10-chloro-5 : 10-dihydrophenarsazine and related compounds can be obtained by direct halogenation and, for this purpose, we have studied the bromination of some typical compounds of this series.

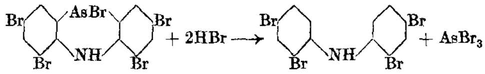
10-Chloro-5 : 10-dihydrophenarsazine in hot glacial acetic acid solution (it is not very soluble in the cold) was treated with bromine (4 mols.), and a colourless well-defined crystalline substance isolated from the cooled solution. Since the nitration of 10-chloro-5 : 10-dihydrophenarsazine produces the 2- and 4-mononitro-derivatives (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1; Gibson and Johnson, J., 1927, 2515), it was anticipated that the fully brominated product would be 10-chloro-2 : 4 : 6 : 8 -tetrabromo-5 : 10-dihydrophenarsazine (I); but the colourless product isolated was arsenic-free and analysis showed it to be tetrabromodiphenylamine. It was

(I.)   (II.)

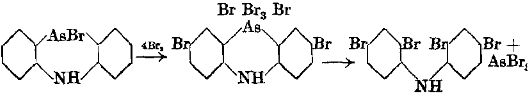
identical with the tetrabromodiphenylamine obtained by brominating diphenylamine under the same conditions. Although the exact constitution of this tetrabromodiphenylamine has not been determined, there can be little doubt from analogy with the well-known tetrachlorodiphenylamine recently synthesised by Chapman (this vol., p. 570) that it is 2 : 4 : 2′ : 4′-tetrabromodiphenylamine (II). Bromination of 10-bromo-5 : 10-dihydrophenarsazine gave the same product.

Under the conditions of the experiment, only four molecular proportions of bromine react with 10-chloro (or bromo)-5 : 10-dihydrophenarsazine and only tetrabromodiphenylamine and not hexabromodiphenylamine is isolated, although the latter compound is obtained when diphenylamine is brominated (in more dilute solution) with six molecular proportions of bromine, tetrabromodiphenylamine being much less soluble than the hexabromo-compound. In view

of this, it was at first thought that the formation of tetrabromodiphenylamine was the result of the reaction (i):

(i) 

This was investigated more closely by carrying out the bromination in acetic acid solution containing an excess of sodium acetate: tetrabromodiphenylamine was still the only isolable product. When the bromination was carried out in cold *o*-dichlorobenzene solution and also in cold carbon tetrachloride solution, hydrogen bromide was evolved as before and a red microcrystalline solid separated in each case. This red substance itself could not be investigated, since it slowly gave off bromine and white fumes, leaving a yellow crystalline solid which proved to be slightly impure tetrabromodiphenylamine. The red substance had the properties of an arsenic perbromide, and, in spite of the probable instability of such a compound at the temperature of boiling acetic acid, the transitory existence of such a substance in the bromination as carried out in the present work may well be assumed. In this case the formation of tetrabromodiphenylamine is explained as follows:

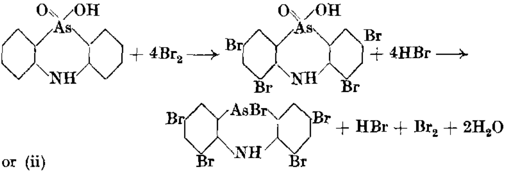


in this scheme hydrogen bromide is not represented as taking part in the production of the tetrabromodiphenylamine. When only two molecular proportions of bromine were used for the bromination of one molecular proportion of 10-bromo-5:10-dihydrophenarsazine, the product contained tetrabromodiphenylamine and unchanged initial material.

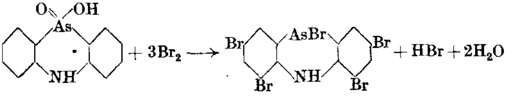
The behaviour towards bromine of some six homologues of 10-chloro-5:10-dihydrophenarsazine in acetic acid solution has also been studied and, in each case, dearsenication of the compound took place with the production of a tetrabromodiphenylamine homologue. The constitution of these bromodiphenylamines is not clear, but the substances, whatever their constitution may be, are identical with the direct bromination products of the diphenylamines as far as we have been able to investigate them.

When phenarsazinic acid was submitted to the action of bromine in hot acetic acid solution, comparatively little hydrogen bromide was evolved, the hot solution acquiring a permanent yellow colour.

As far as the experimental conditions allowed them to be determined, three molecular proportions appeared to be the amount required for each molecular proportion of the acid. The main product of this reaction was the tetrabromodiphenylamine already mentioned, 2 : 4 : 6 : 8 : 10 - *pentabromo* - 5 : 10 - *dihydrophenarsazine* being obtained in smaller quantity, and 2 : 4 : 6 : 8-*tetrabromophenarsazinic acid* (there seems every reason for assuming these constitutions) in still less quantity. It is suggested that the formation of the pentabromodihydrophenarsazine is explained by equation (ii). This

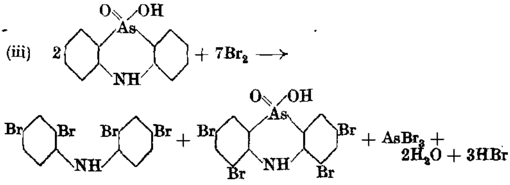


or (ii)



reaction involves hydrogen bromide acting as a reducing agent; another example of this has already been indicated (this vol., p. 782); 3-nitro-*o*-tolylarsinic acid when boiled in a concentrated solution of hydrogen bromide oxidises the latter to bromine. The stability of the pentabromodihydrophenarsazine towards hydrogen bromide (although an aqueous solution was used) and acetic acid may be regarded as evidence against hydrogen bromide playing a part in the production of tetrabromodiphenylamine as was first suggested.

(iii)



It is suggested that the production of tetrabromodiphenylamine and in less quantity of tetrabromophenarsazinic acid is represented by equation (iii), which summarises reactions consisting of (*a*)

bromination of phenarsazinic acid to a dibromophenarsazinic acid, (*b*) reduction of part of the latter to tribromo-5 : 10-dihydrophenarsazine, (*c*) the action of bromine on this, yielding tetrabromodiphenylamine and arsenious bromide, and (*d*) further bromination of part of the dibromophenarsazinic acid to tetrabromophenarsazinic acid. Actually this equation does not represent the final stage, because there is still the probability of the hydrogen bromide and the tetrabromophenarsazinic acid reacting to produce 2 : 4 : 6 : 8 : 10-pentabromo-5 : 10-dihydrophenarsazine and bromine by reduction, and the action of this bromine on the original compound, so that the relative amount of tetrabromodiphenylamine will be greater than that indicated. This explanation of the reactions taking place is in substantial agreement with the experimental results.

2 : 4 : 6 : 8 : 10-Pentabromo-5 : 10-dihydrophenarsazine is readily oxidised by hydrogen peroxide to 2 : 4 : 6 : 8-tetrabromophenarsazinic acid. This also is a stable substance and identical with that isolated in small quantity from the mixture of products of the action of bromine on phenarsazinic acid in hot acetic acid solution.

Direct halogenation of aromatic arsenical compounds frequently leads to dearsenication, and the action of potassium iodide and dilute sulphuric acid has been used in orienting these substances, the arsenic group being replaced by an iodine atom. On the other hand, Michaelis (*Annalen*, 1902, **320**, 334) has shown that 2 : 4-dimethylphenyldichloroarsine when chlorinated in aqueous suspension yields a mono- and a di-chloro-2 : 4-dimethylphenylarsinic acid; Bertheim (*Ber.*, 1910, **43**, 531) also showed that acetyl-*p*-arsanilic acid and *p*-arsanilic acid can be directly halogenated, and Fisher and Raiziss (*J. Amer. Chem. Soc.*, 1929, **51**, 529) have brominated 3-nitro-4-hydroxyphenylarsinic acid.

It would appear from the present work that bromination of compounds of the phenarsazine type (which may be considered to be derivatives of *o*-aminophenylarsinic acid) is accompanied by dearsenication, bromine replacing the arsenic group. The reaction belongs, therefore, to the same class as that of the action of halogens on aromatic compounds generally, causing a direct replacement of a substituting group. The production of 2 : 4 : 6-tribromoaniline by the action of bromine on sulphanilic acid (Heinrichen, *Annalen*, 1889, **253**, 268) has long been known and a summary of the more important typical examples of bromine replacement has been given by Sudborough and Lakhumalani (*J. Ind. Inst. Sci.*, 1914—1918, I, 133).

EXPERIMENTAL.

Bromination of 10-Chloro-5 : 10-dihydrophenarsazine.—A boiling solution of 10-chloro-5 : 10-dihydrophenarsazine (5·55 g.) in glacial

acetic acid (222 c.c.) was treated with bromine (4 c.c.; 4 mols.) drop by drop. The colour of the bromine was immediately discharged and hydrogen bromide evolved in considerable quantity. The liquid was boiled for some time to drive off as much as possible of the hydrogen bromide. Even while hot, colourless needles began to separate, and these almost filled the cold solution. The solid product after recrystallisation from glacial acetic acid (charcoal) had m. p. 186° (Found: Br, 65·1. Calc.: Br, 66·0%) and was identical with the tetrabromodiphenylamine, m. p. 186°, obtained from diphenylamine (4·2 g.), boiling glacial acetic acid (300 c.c.), and bromine (5 c.c.; 4 mols.) under the same conditions.

Hexabromodiphenylamine was prepared by treating diphenylamine (16·9 g.) in boiling acetic acid (1183 c.c., this large volume being necessary on account of the sparing solubility of tetrabromodiphenylamine) with bromine (30 c.c.; 6 mols., the last 2 mols. of which were less rapidly absorbed). The greenish crystalline product which separated on cooling was twice crystallised from benzene (charcoal) and obtained in colourless prisms, m. p. 221—222° (Gnehm, *Ber.* 1875, **8**, 926, gives m. p. 218°). The melting points of this and some of the other brominated diphenylamines described in this communication are not very sharp, softening taking place before the substances actually melt.

Bromination of 10-*Bromo*-5 : 10-*dihydrophenarsazine*.—10-Bromo-5 : 10-dihydrophenarsazine (10 g.) in acetic acid (250 c.c.) was treated with bromine (6·2 c.c.; 4 mols.) under exactly similar conditions. More bromine than the above was not absorbed and was simply expelled with hydrogen bromide from the boiling solution. The product was identical with the tetrabromodiphenylamine described above (Found: Br, 66·7%).

Bromination of 10-*Chloro*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*.—The quantities used were: chloro-compound (6·11 g.), glacial acetic acid (420 c.c.), bromine (4 c.c.; 4 mols.), and the reaction was carried out in the same manner. The first half of the bromine reacted more readily than the second half. The greater part of the solvent was distilled off, and the product recrystallised from acetic acid. To obtain it colourless and free from the merest trace of arsenic it was necessary to add a few drops of hydrogen peroxide to the acetic acid; experience has shown that the yellow colour was probably due to a small quantity of the intermediate bromo-compound of the chloro-phenarsazine which had escaped the action of further bromine. The product crystallised in colourless flat plates, m. p. 161—162° (Found: Br, 61·4. Calc.: Br, 62·3%). Although the melting point of the compound was somewhat low, it did not depress the melting point (166°) of the product obtained whe

di-*p*-tolylamine (3·94 g.) in acetic acid (78 c.c.) was treated with bromine (4 c.c.; 4 mols.) under similar conditions, which undoubtedly was tetrabromodi-*p*-tolylamine (Found: Br, 61·6%) (*Ber.*, 1880, **13**, 1545).

Bromination of 7-*Chloro*-12 : 7-*dihydrobenzophenarsazine*.—The chloro-compound (13 g.), dissolved in boiling acetic acid (786 c.c.), was treated with bromine (8 c.c.; 4 mols.), and the product worked up in the usual manner. The *tetrabromophenyl-α-naphthylamine* obtained formed colourless needles, m. p. 150° (Found: Br, 59·8. $C_{16}H_{11}NBr_4$ requires Br, 59·8%), and was identical with the product obtained by treating phenyl-α-naphthylamine (4·38 g.) in boiling acetic acid solution (220 c.c.) with bromine (4 c.c.; 4 mols.).

Bromination of 12-*Chloro*-7 : 12-*dihydrobenzophenarsazine*.—This chloro-compound (6·5 g.) was dissolved as far as possible in boiling acetic acid (650 c.c.) and treated with bromine (4 c.c.; 4 mols.) in tbe usual manner. The colourless silky needles which separated had m. p. 205°, and this remained unchanged when the substance was recrystallised from acetic acid and then three times from benzene. Several specimens were analysed (Found: Br, 56·0, 57·7, 56·4, 55·5, 56·7, 56·45. Calc. for tetrabromophenyl-β-naphthylamine: Br, 59·8%. Calc. for tribromophenyl-β-naphthylamine: Br, 52·6%). The product was free from arsenic. A tetrabromophenyl-β-naphthylamine, m. p. 202—203°, has been described by Zincke and Lawson (*Ber.*, 1887, **20**, 1170).

Bromination of 7-*Chloro*-9-*methyl*-7 : 12-*dihydrobenzophenarsazine*.—The chloro-compound (6·85 g.), dissolved in boiling acetic acid (544 c.c.), readily absorbed bromine (4 c.c.; 4 mols.). The resulting solution deposited pale hrown plates. This product was recrystallised from acetic acid and, although the final product was free from arsenic, it still retained a small amount of colour. It had m. p. 167—170° (Found: Br, 57·8. Calc.: Br, 58·25%), and was identical with the tetrabromo-*p*-tolyl-α-naphthylamine obtained by treating *p*-tolyl-α-naphthylamine (4·66 g.) in boiling acetic acid solution (150 c.c.) with bromine (4 c.c.; 4 mols.) (*J. pr. Chem.*, 1901, **64**, 510).

Bromination of 12-*Chloro*-10-*methyl*-7 : 12-*dihydrobenzophenarsazine*.—The tetrabromo-*p*-tolyl-β-naphthylamine which crystallised from the solution obtained by adding bromine (4 c.c.; 4 mols.) to the chloro-compound (6·85 g.) in boiling acetic acid (500 c.c.) was isolated in colourless silky needles, m. p. 165° (Found: Br, 58·6. Calc.: Br, 58·25%). It was identical with the tetrabromo-*p*-tolyl-β-naphthylamine obtained by brominating *p*-tolyl-β-naphthylamine as described for the isomeric substance (compare Friedländer, *Ber.*, 1883, **16**, 2078; bromination in carbon disulphide solution).

Bromination of 10-*Chloro*-5 : 10-*dihydrophenarsazine in* o-*Dichlorobenzene and in Carbon Tetrachloride at the Ordinary Temperature.*—When the chloro-compound (2·0 g. in 200 c.c. of *o*-dichlorobenzene or 1·4 g. in 300 c.c. of carbon tetrachloride) was treated with bromine (1·44 c.c. and 1 c.c., respectively; 4 mols.), hydrogen bromide was evolved and a red crystalline material separated. This was filtered off and washed with the solvent. On exposure to air, it lost bromine and left a yellow solid, from which, after recrystallisation from acetic acid or from acetone, only tetrabromodiphenylamine was obtained.

After 2 : 4 : 2′ : 4′(?)-Tetrabromodiphenylamine (9·7 g.), arsenious chloride (7·3 g.), and *o*-dichlorobenzene (25 c.c.) had been boiled for 14 hours, only unchanged materials were isolated.

Bromination of 10-*Bromo*-5 : 10-*dihydrophenarsazine in Presence of Sodium Acetate.*—The bromo-compound (2·0 g.) together with fused sodium acetate (5·0 g.) was dissolved in boiling acetic acid (50 c.c.), and the mixture treated with bromine (1·24 c.c.; 4 mols.). No hydrogen bromide was evolved, but crystalline material (inorganic) separated. The hot filtrate from this deposited tetrabromodiphenylamine (m. p. 186°) on cooling.

Bromination of Phenarsazinic Acid: Isolation of 2 : 4 : 6 : 8 : 10-*Pentabromo*-5 : 10-*dihydrophenarsazine.*—The following description is typical of several experiments. Phenarsazinic acid (11 g.) in boiling acetic acid (350 c.c.) was treated slowly with bromine (6 c.c.: 3 mols.). The bromine was decolourised, the liquid became yellow, and only a small quantity of hydrogen bromide was evolved. At the same time a yellow crystalline solid began to separate and after the addition of the bromine was completed it was separated from the boiling solution. The filtrate deposited tetrabromodiphenylamine in long needles on cooling. The yellow solid was repeatedly extracted with boiling acetic acid, in which it was only sparingly soluble, and so obtained free from tetrabromodiphenylamine. Finally it was recrystallised from benzene, in which also it was sparingly soluble, but more soluble than in acetic acid.

2 : 4 : 6 : 8 : 10-*Pentabromo*-5 : 10-*dihydrophenarsazine* (the yield varied from 2·5 to rather more than 4 g. in different experiments) was thus obtained in yellow needles, m. p. 275° (Found: C, 23·1; H, 1·0; N, 2·3; Br, 62·6, 62·6; As, 11·7, 11·6.* $C_{12}H_5NBr_5As$

* Owing to the possibility of loss of volatile arsenic halide during the estimation of arsenic in this compound of high bromine content by the ordinary method, the determination of arsenic (and of bromine) was carried out as follows: The substance (about 0·6 g.) was heated in a sealed tube at 200—255° with fuming nitric acid (2 c.c.) and silver nitrate (about 1 g.) for 7 hours. The diluted contents of the tube were washed through a Gooch crucible, the silver halide was collected and weighed, and the filtrate and washings were

requires C, 22·6; H, 0·8; N, 2·2; Br, 62·7; As, 11·8%). The compound is not affected when boiled with a mixture of concentrated hydrobromic acid and acetic acid, and does not appear to be acted upon by bromine in acetic acid solution.

During the crystallisation of the pentabromo-compound from benzene, a colourless substance remained undissolved. It was obtained only in small quantity and proved to be 2 : 4 : 6 : 8-tetrabromophenarsazinic acid, described below.

2 : 4 : 6 : 8-*Tetrabromophenarsazinic Acid*.—The preceding substance (2·0 g.) in acetic acid (160 c.c.) was treated with hydrogen peroxide (20 vols.; 14 c.c.), and the mixture heated to boiling. Bromine was evolved and the yellow colour of the solid disappeared. Water (200 c.c.) was added and the mixture allowed to cool. The solid was filtered off and dissolved in boiling very dilute aqueous sodium hydroxide. The hot filtered solution was mixed with 20% aqueous sodium hydroxide until it just remained clear at the boiling point. On cooling, sodium 2 : 4 : 6 : 8-tetrabromophenarsazinate crystallised in colourless soft plates. It was dissolved in water, and the free *acid* precipitated as a somewhat gelatinous mass by the addition of hydrochloric acid. The acid crystallised from 90% acetic acid in colourless needles which began to decompose at about 294° (Found : Br, 54·2. $C_{12}H_6O_2NBr_4As$ requires Br, 54·1%).

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E. 1. [*Received, March 26th*, 1929.]

CXLIV.—3 : 4-*Methylenedioxyphenylarsinic Acid.*

By ISIDORE ELKANAH BALABAN.

THE only available method for the preparation of 3 : 4-dihydroxyphenylarsinic acid is described in D.R.-P. 271892, the yield being extremely poor; Fargher (J., 1920, **117**, 865) also found the method unsatisfactory, and attempted to obtain the acid by demethylation of 3 : 4-dimethoxyphenylarsinic acid. The desirability of preparing the acid and some of its derivatives and examining them for trypanocidal action led the author to investigate various modes of synthesis.

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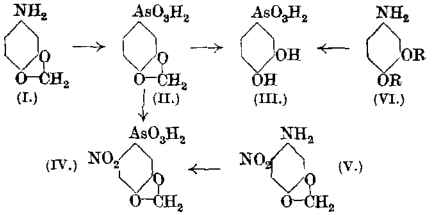
concentrated to about 20 c.c. in a large Kjeldahl flask. After cooling, 6 c.c. of concentrated sulphuric acid were added and the liquid was heated until free from nitric acid. The liquid was then diluted to about 150 c.c. and saturated with sulphur dioxide, and the excess of the latter boiled off. Slightly more than sufficient dilute hydrochloric acid was added to precipitate the excess of silver and then the solution was made just alkaline (phenolphthalein) with sodium hydroxide and thereafter just acid with sulphuric acid, and about 3 g. of sodium bicarbonate were added. The solution was then titrated against standard iodine (0·1*N*) with starch as indicator.

It has been reported (Balaban, J., 1928, 809) that 4-aminopyrocatechol failed to undergo the Bart–Schmidt reaction. The following schemes suggested a possible synthesis :



4-Aminopyrocatechol methylene ether (I) is most conveniently prepared by Hesse's method (*Annalen*, 1879, **199**, 341), since reduction of 4-nitropyrocatechol does not proceed smoothly, and the Hofmann reaction with piperonylamide (Rupe and Majewski, *Ber.*, 1900, **33**, 3403) gives but a poor yield. The ether affords a means of obtaining 3 : 4-*methylenedioxyphenylarsinic acid* (II). Three methods for opening the methylenedioxy-ring were unsuccessfully applied to this acid and to its nitro-derivative described below, *viz.*, the use of (*a*) thionyl chloride (Barger, J., 1908, **93**, 563), (*b*) sulphuric acid in the presence of a phenol (Späth and Quietensky, *Ber.*, 1927, **60**, 1882), and (*c*) anhydrous aluminium chloride in chlorobenzene solution (Mauthner, *J. pr. Chem.*, 1928, **119**, 74); though evidence of the formation of a pyrocatechol derivative was obtained, no arsinic acid could be isolated.

The nitro-acid obtained on nitration of (II) is 6-*nitro*-3 : 4-*methylenedioxyphenylarsinic acid* (IV), for it is identical with the nitro-acid prepared from 5-nitro-4-aminopyrocatechol methylene ether (V) : its production is another instance showing that disubstituted pyrocatechol methylene ethers are 4 : 5-derivatives (compare Jones and Robinson, J., 1917, **111**, 904). Reduction of the nitro-acid gave the *corresponding amino-acid*. This and other derivatives were tested in experimental trypanosomiasis : the results are shown in the table below. Unsuccessful attempts were made to prepare 6-hydroxy-3 : 4-methylenedioxyphenylarsinic acid from the corresponding amino-acid, and also 4-hydroxypyrocatechol methylene ether (briefly mentioned by Malagnini and Armani, *Chem.-Ztg.*, 1907, 884) and 5-nitro-4-hydroxypyrocatechol methylene ether by the usual methods; in the last case a poor yield of 4-nitropyrocatechol methylene ether was obtained.

4-*Nitro*-1 : 2-*diacetoxybenzene*, prepared by acetylation of 4-nitropyrocatechol, gave on reduction 4-*amino*-1 : 2-*diacetoxybenzene* (VI; R = CO·CH_3). This diazotised normally, and the diazo-solution reacted with sodium arsenite in acid solution with the evolution of much gas, but no arsinic acid could be isolated. The acid solution gave with ferric chloride the green coloration characteristic of pyrocatechol derivatives.

4-*Nitropyrocatechol dibenzyl ether* was reduced to 4-*aminopyrocatechol dibenzyl ether* (VI; R = CH_2Ph), but no arsinic acid could be obtained from this in numerous experiments.

Phenylarsinic acids.	*T.*	*C.*	*C/T.*
3 : 4-Methylenedioxy- (*o*)	0·1	0·1	1·0
(*i*)	0·05	0·05	1·0
6-Amino-3 : 4-methylenedioxy- (*i*)	0·25	0·25	1·0
6-Acetamido-3 : 4-methylenedioxy- (*i*)	0·5	0·5	1·0
Arsenobenzenes.			
3 : 4 : 3′ : 4′-Dimethylenedioxy- (*o*)	2·0	2·0	1·0
6 : 6′-Diamino-3 : 4 : 3′ : 4′-dimethylenedioxy- (*o*)	2·0	1·0	1/2

(Administration : *o* = per os, *i* = intravenous.)

EXPERIMENTAL.

3 : 4-*Methylenedioxyphenylarsinic Acid* (II).—25 G. of 4-aminopyrocatechol methylene ether hydrochloride in 16% hydrochloric acid (100 c.c.) at 0° were diazotised with 22·0 c.c. of 10% sodium nitrite solution, added to sodium arsenite solution (arsenious oxide, 18·0 g.; sodium hydroxide, 20·0 g.; water, 200 c.c.), and heated on the water-bath. The filtered liquid, after being acidified (Congo-red) with concentrated hydrochloric acid, slowly deposited 14·7 g. (yield, 41·7%) of 3 : 4-*methylenedioxyphenylarsinic acid.* This acid crystallises from boiling water, in which it is moderately easily soluble, in colourless silky rhomboids containing $\frac{1}{2}H_2O$, which decompose at 270° after previous darkening (Found : loss at 100°, 5·1; As, 28·8. $C_7H_7O_5As,\frac{1}{2}H_2O$ requires H_2O, 5·2; As, 28·9%). It is soluble in cold 80% formic acid and moderately easily soluble in glacial acetic acid and hot alcohol. The calcium salt forms bunches of fine needles, the barium salt is microcrystalline, and the magnesium salt is amorphous. The acid is extremely stable towards boiling concentrated hydrochloric acid and 25% sodium hydroxide solution. On reduction with sodium hydrosulphite at 60°, *arsenopyrocatechol methylene ether* (yield, 65%) was obtained as a pale yellow, amorphous, insoluble powder (Found : As, 37·5. $C_{14}H_{10}O_4As_2$ requires As, 38·2%).

Nitration of 3 : 4-*Methylenedioxyphenylarsinic Acid.*—The acid (30·75 g.) was nitrated at 0°, and the solution poured on ice and

made just acid to Congo-red with anhydrous sodium carbonate; 21·6 g. (yield, 59·5%) of *6-nitro-3 : 4-methylenedioxyphenylarsinic acid* (IV) were then obtained. The nitro-acid crystallises from 2*N*-acetic acid, in which it is moderately easily soluble, in pale brown, anhydrous spikes, and from water, in which it is very sparingly soluble, in short stout prisms, m. p. 231° (decomp.) (Found in air-dried material: As, 25·4; N, 5·0. $C_7H_6O_7NAs$ requires As, 25·7; N, 4·8%). It is insoluble in alcohol. The magnesium salt is amorphous, the calcium salt forms irregular transparent plates, and the barium salt is microcrystalline.

When 5-nitro-4-aminopyrocatechol methylene ether (Jones and Robinson, *loc. cit.*) is submitted to the Bart–Schmidt reaction, the above nitro-acid is obtained (yield, 36·9% or, allowance being made for recovered initial material, 73·8%). When prepared by this method, it crystallises from water in long, bright yellow, rectangular, anhydrous prisms, m. p. 228° (decomp.) (Found: As, 25·5; N, 4·9%).

The acid from both sources is very stable towards boiling concentrated hydrochloric acid. When heated with 25% sodium hydroxide solution, it gives an intense blood-red solution, from which no products have been isolated. When it is heated with 8% sodium hydroxide solution for 15 minutes, the same colour is produced, but the material obtained now crystallises in diamond-shaped prisms and gives no coloration with ferric chloride (whereas the mother-liquor gives an intense green), has m. p. 225° (decomp.), and gives on analysis the results required for the initial material (compare Jones and Robinson). 4-Bromo-5-nitropyrocatechol methylene ether also produces the blood-red colour under similar conditions, but again no product can be isolated.

6-Amino-3 : 4-methylenedioxyphenylarsinic Acid.—The nitro-acid (18·7 g.) was reduced at 70° with ferrous sulphate (yield, 10·18 g.; 60·5%). The *amino-acid* crystallises from boiling water, in which it is moderately easily soluble, in long, colourless, fine, silky, anhydrous needles (Found: As, 29·1; N, 5·1. $C_7H_8O_5NAs$ requires As, 28·7; N, 5·4%). It is readily soluble in 2*N*-hydrochloric acid and diazotises normally, is soluble in 80% formic acid and moderately easily soluble in acetic acid, but almost insoluble in alcohol. The magnesium salt is amorphous and the calcium salt forms irregular prisms.

6 : 6′-Diaminoarsenopyrocatechol methylene ether was prepared by reduction of the above acid and obtained as a bright yellow, amorphous powder, soluble in hydrochloric acid (Found: As, 33·3. $C_{14}H_{12}O_4N_2As_2$ requires As, 35·5%).

6-Acetamido-3 : 4-methylenedioxyphenylarsinic acid was obtained

by acetylation in alkaline solution of the corresponding amino-acid, and crystallised from 2*N*-acetic acid in colourless, rectangular, anhydrous prisms (Found in different samples: As, 24·5, 24·5; N, 4·1, 4·2. $C_9H_{10}O_6NAs$ requires As, 24·7; N, 4·6%). It is moderately easily soluble in water, but sparingly soluble in glacial acetic acid. The magnesium salt is amorphous.

4-*Nitro*-1 : 2-*diacetoxybenzene*.—A mixture of 4-nitropyrocatechol (15·5 g.), acetic anhydride (31 c.c.), and sulphuric acid (2 c.c.) was heated for ½ hour on the water-bath and poured on ice. The product (22 g.; yield, 92%) crystallised from 95% alcohol (charcoal) in colourless rectangular prisms, m. p. 98° (Found: N, 6·0. $C_{10}H_9O_6N$ requires N, 5·8%). It is moderately easily soluble in boiling water, readily soluble in alcohol, ether, chloroform, benzene, and acetone, and readily hydrolysed by cold 2*N*-sodium hydroxide, but only slowly by hot dilute hydrochloric acid.

4-*Amino*-1 : 2-*diacetoxybenzene* (VI; R = $CO{\cdot}CH_3$) can be obtained by reducing the nitro-compound with iron and water (1 drop of acetic acid), but is more conveniently prepared by Bell and Kenyon's method (*J.*, 1926, 954). The nitro-compound (5·0 g.) in moist ether (70 c.c.) is treated with aluminium amalgam (1·5 g.), and the reaction started by warming on the water-bath. After 3 hours, the ether, together with washings, is removed and 2·2 g. (yield, 41·8%) of product obtained, crystallising from 95% alcohol in thick prisms, m. p. 114° (Found: N, 6·6, 6·55. $C_{10}H_{11}O_4N$ requires N, 6·7%). It is sparingly soluble in hot water, readily soluble in alcohol, acetone, and chloroform, and somewhat less soluble in benzene and ether. It dissolves readily in dilute hydrochloric acid and diazotises normally. The *N*-acetyl derivative crystallises from water (moderately easily soluble) in diamond-shaped plates, m. p. 144°.

4-*Nitropyrocatechol Dibenzyl Ether*.—A mixture of 4-nitropyrocatechol (15·5 g.), sodium hydroxide (8 g.), and benzyl chloride (26 g.) in absolute alcohol (300 c.c.) was heated for 15 hours on the steam-bath, the alcohol removed, and the residue extracted with *N*-sodium hydroxide solution; 16·3 g. (yield, 48·7%) of the *dibenzyl* ether were obtained, which crystallised from 95% alcohol (charcoal) in long, fine, colourless needles, m. p. 97° (Found: N, 4·4. $C_{20}H_{17}O_4N$ requires N, 4·2%). It is very sparingly soluble in alcohol, but readily soluble in acetone, benzene, chloroform, and ether, and is only slowly hydrolysed to the phenol by concentrated hydrochloric acid. It is unaffected by sodium hydroxide.

4-*Aminopyrocatechol Dibenzyl Ether* (VI; R = CH_2Ph).—The above nitro-compound can be reduced by West's method (*J.*, 1925, 127, 494) or by that of Bell and Kenyon (*loc. cit.*), the yield

being about 50% in both cases; the *amine* crystallises from chloroform in laminæ, m. p. 92° (Found: N, 4·8. $C_{20}H_{19}O_2N$ requires N, 4·6%). It is moderately easily soluble in alcohol and readily soluble in acetone, benzene, chloroform, and ether. The hydrochloride crystallises from dilute hydrochloric acid, in which it is almost insoluble in the cold, in colourless needles, m. p. 197°; the solution diazotises normally. The acetyl derivative forms colourless rods from alcohol (moderately easily soluble), m. p. 150°.

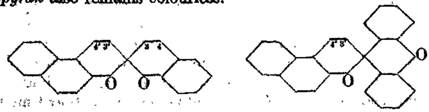
The author is indebted to Mr. R. H. Klein, F.I.C., and to Mr. J. G. Everett, B.Sc., A.I.C., for the analytical and the biological data respectively.

Research Laboratory, Messrs. May & Baker, Ltd.,
Wandsworth, S.W. 18. [*Received, March 16th*, 1929.]

CXLV.—*Styrylpyrylium Salts. Part XII.* spiro*Pyrans derived from 9-Methyl- and 9-Ethyl-xanthylium Salts.*

By Francis Irving.

It has been shown by Atkinson and Heilbron (J., 1926, 676) that the 9-styrylxanthylium salts are strictly analogous in their colour reactions to the 2-styrylbenzopyrylium derivatives (Buck and Heilbron, J., 1922, **121**, 1198). A study has now been made of the condensation of 9-methyl- and 9-ethyl-xanthylium chloride with *o*-hydroxy-aldehydes and of the *spiro*pyrans produced on hydrolysis, in order to compare the latter compounds with the benzonaphtha-*spiro*pyrans. Dickinson and Heilbron (J., 1927, 1699) have shown that only *spiro*pyrans having at least one of the pyran rings attached to a naphthalene nucleus have the power of forming coloured ions on the application of heat and, further, that this only occurs when this pyran ring is unsubstituted in the 3′-position (I). *Xantha*-β-*naphtha*spiro*pyran* (II) fulfils the above conditions and, as was anticipated, develops a strawberry colour when heated in hot diphenyl ether and also when melted; in both cases the colour disappears on cooling. On the other hand, 3′-*methylxantha*-β-*naphtha*spiro*pyran*, which is analogous to 3′-methylbenzo-β-naphtha*spiro*pyran, fails to give a colour on heating; *benzoxantha*-spiro*pyran* also remains colourless.

(I.)  (II.)

The xanthylium salts from which these *spiro*pyrans are derived are less stable than the corresponding pyrylium compounds; for instance, in the condensation of 2-naphthol-1-aldehyde with 9-methylxanthenol in ethereal solution by means of dry hydrogen chloride a mixture of the xanthylium salt and the *spiro*pyran was obtained but with 9-ethylxanthenol, 3′-methylxantha-β-naphtha*spiro*pyran alone separated (compare Dickinson, Heilbron, and O'Brien, J. 1928, 2077). The *spiro*pyrans themselves are reconverted into the xanthylium salts only with difficulty; they give xanthylium salt colorations, not with glacial acetic acid, but only when trichloroacetic acid is used.

EXPERIMENTAL.

*Xantha-β-naphtha*spiro*pyran* (II).—To a dry solution of 9-methylxanthenol prepared from xanthone (10 g.) by Atkinson and Heilbron's method (*loc. cit.*), the theoretical quantity of 2-naphthol-1-aldehyde (8·5 g.) was added, and a slow stream of hydrogen chloride introduced. The yellow solution gradually darkened and an oil separated and then redissolved, an intense green solution being finally obtained. On standing in the cold for 48 hours a mixture of small bronze crystals and larger, faintly coloured prisms crystallised. These were separated by means of acetone, in which the latter product (the spiro*pyran*) was almost insoluble. The acetone and ether mother-liquors gave a further quantity of the *spiro*pyran on treatment with dilute ammonia until the colour was discharged. This substance on recrystallisation from benzene gave small colourless crystals which melted at 201° to a deep red liquid, the colourless *spiro*pyran again being formed on solidification. The solution of the compound in boiling xylene was colourless, but in boiling veratrole a faint strawberry tinge developed, and by using boiling diphenyl ether as solvent a deep strawberry colour, which disappeared on cooling, was obtained. In cold glacial acetic acid no colour was observed, but on boiling, a very faint pink colour, which faded on cooling, was produced; the addition of trichloroacetic acid to the solution in glacial acetic acid gave rise to an intense green xanthylium salt coloration (Found: C, 86·5; H, 4·7. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%).

*Benzoxantha*spiro*pyran*.—The theoretical quantity of salicylaldehyde (6·5 g.) was added to a dry solution of 9-methylxanthenol prepared from xanthone (10 g.), and a slow stream of hydrogen chloride introduced. A red oil rapidly separated and then redissolved as the solution became saturated, a deep purple solution resulting. As no chloride separated after long standing at 0°, perchloric acid (9 c.c. of 70%) was added and in a short time large

purple needles with a bronze reflex began to appear. After 2 days the salt was removed and hydrolysed by means of dilute aqueous ammonia in presence of ether. The crude spiro*pyran* obtained on evaporation of the ethereal layer was recrystallised several times *from acetone (charcoal), giving colourless prisms (faintly yellow* when viewed in bulk), m. p. 154°, sparingly soluble in acetone, alcohol, or cold glacial acetic acid (Found: C, 84·6; H, 4·7. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). Its solutions in boiling diphenyl ether and in boiling dodecahydrosqualene (over 300°) were colourless. In hot glacial acetic acid also it gave a colourless solution, but on the addition of trichloroacetic acid a purple xanthylium salt coloration was produced.

3′-*Methylxantha*-β-*naphtha*spiro*pyran*.—A solution of xanthone (10 g.) in boiling benzene (85 c.c.) was slowly treated with an ethereal solution of magnesium ethyl iodide prepared from ethyl iodide (28 g.). An orange colour developed immediately and a yellow solid was deposited, this dissolving again as more Grignard reagent was added. After refluxing for 1½ hours, the solvent was distilled off and the thick residue decomposed by the addition of ice-water. The product (9-ethylxanthenol) was removed by ether extraction. After the ethereal solution, which was assumed to contain the theoretical amount of product, had been dried, 2-naphthol-1-aldehyde (8·5 g.) was added, and the whole saturated with dry hydrogen chloride; an oil then separated, redissolving later to a solution which was purple when viewed in thin layers and deep red in bulk. On standing over-night at 0°, a considerable amount of colourless crystalline substance separated which after recrystallisation from benzene had m. p. 271°. Solutions of this *compound* in boiling diphenyl ether or glacial acetic acid were colourless, but the addition of trichloroacetic acid to the latter solution gave an intense green coloration (Found: C, 86·1; H, 4·8. $C_{26}H_{18}O_2$ requires C, 86·2; H, 5·0%).

The author wishes to express his indebtedness to Professor I. M. Heilbron, D.S.O., for valuable advice and encouragement given while this research was in progress.

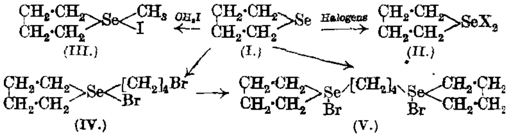
THE UNIVERSITY, LIVERPOOL. [*Received, March* 28*th*, 1929.]

CXLVI.—*Heterocyclic Systems containing Selenium. Part I.* cyclo*Selenobutane* (*Tetrahydroselenophen*).

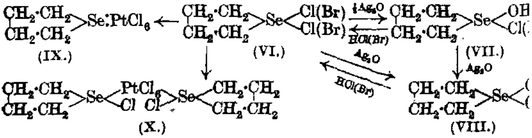
By Gilbert T. Morgan and Francis Hereward Burstall.

In the course of a systematic investigation on cyclic derivatives o selenium we have prepared cyclo*selenobutane* (*tetrahydroselenophen* formula I) by condensing tetramethylene dibromide and sodiun selenide, using special precautions to avoid oxidation of the alkal selenide. This reaction is applicable to the production of othe cyclic systems containing selenium, but the present communicatio deals only with a description of *cyclo*selenobutane and its derivatives

As a compound containing bivalent selenium, *cyclo*selenobutan exhibits considerable residual affinity. It combines additively wit mercuric chloride and the halogens and with alkyl halides an alkylene dihalides. These reactions are summarised in the followin diagram :



The three crystalline cyclo*selenobutane* 1 : 1-*dihalides* (II) show a decrease in solubility in organic media and a colour gradatio (colourless–yellow–purple-black) as the atomic weight of th halogen increases. The solubility of these dihalides in non-hydroly ing organic media points to a non-polar character, but in hot wate the dichloride and dibromide dissolve to give strongly acid solution from which they crystallise unchanged on cooling. These reaction suggest a change in the molecular structure of the dissolved dihalide on which some light is thrown by the experiments indicated in th following diagram :



Moist silver oxide with excess of dichloride or dibromide (VI) yields a cyclo*selenibutane* 1-*hydroxychloride* or 1-*hydroxybromide*

(VII). These hydroxyhalides are colourless crystalline salts which dissolve freely in water, yielding acid solutions, but are almost insoluble in non-hydrolysing solvents. By addition of the appropriate hydrogen halide they are reconverted into dichloride or dibromide.

With excess of silver oxide the foregoing hydroxyhalides and dihalides yield *cyclo*selenibutane 1 : 1-dihydroxide (VIII), a very soluble hygroscopic substance which dissolves in water to a feebly acid solution (p_H 6·0 to 6·2) and behaves as an amphoteric hydroxide.

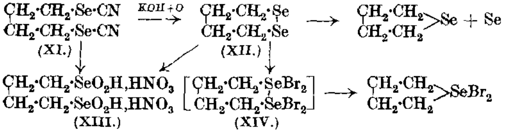
In cold dilute solution combination occurs between molecular proportions of the dichloride and platinic chloride so that a simple chloroplatinate (IX) is formed which, although sparingly soluble in water, dissolves in the ordinary organic media, including the alcohols, acetone, benzene, and chloroform. With warm concentrated solutions a more complex chloroplatinate (X) is obtained, which is readily soluble in water or alcohol, but insoluble in acetone, benzene, and other organic media.

cyclo*Selenibutane 1-chloroplatinate* (IX) behaves like the non-polar *cyclo*selenibutane dihalides in dissolving in non-hydrolysing organic media, whereas *bis-1-chloro*cyclo*selenibutane 1-chloroplatinate* (X) is evidently a polar compound, dissolving in water and corresponding with the hydrolysed forms of the dihalides in aqueous solution.

Water-soluble selenonium salts are produced when *cyclo*selenobutane combines with alkyl halides and alkylene dihalides. With methyl iodide cyclo*selenibutane 1-methiodide* is produced, whereas the interaction with $\alpha\delta$-butylene dibromide proceeds in two stages, giving successively *1-δ-bromobutyl*cyclo*selenibutane 1-bromide* (IV) and *tetramethylene-αδ-bis*cyclo*selenibutane* 1 : 1'-*dibromide* (V). These selenium salts furnish neutral aqueous or alcoholic solutions, from which silver nitrate readily precipitates the halogen ion.

An alternative method of obtaining *cyclo*selenobutane and its derivatives has been devised starting from tetramethylene dibromide and potassium selenocyanate, which interact smoothly to yield *tetramethylene diselenocyanate* (XI). Hydrolysis of this substance by alcoholic potash or soda, accompanied by aerial oxidation, leads to cyclo*tetramethylene diselenide* (cyclo*diselenobutane*; XII) and when heated the diselenide loses half its selenium and passes into *cyclo*selenobutane, whereas bromine and the diselenide interact to give *cyclo*selenibutane dibromide, the eliminated selenium being obtained as such or as its monobromide according to the amount of bromine employed. This conversion of diselenide into *cyclo*selenibutane dibromide is preceded by the intermediate formation of an

unstable orange tetrabromide (XIV). The structure of this cyclic diselenide is revealed by its quantitative conversion with excess of nitric acid into *tetramethylenediseleninic acid dinitrate* (XIII), a substance which is also obtained on heating tetramethylene diselenocyanate (XI) with the same oxidising agent.



We are indebted to Dr. Sugden for his kind assistance in the following determination of the parachor of *cyclo*selenobutane.

t	10°	20°	30°	40°
Surface tension, γ	41·28	39·53	38·07	37·14
Density, *D*	1·493	1·478	1·463	1·452
Parachor	229·4	229·3	229·5	229·8
Mean	229·5	Calculated	227·3	

These results show that *cyclo*selenobutane is quite normal as regards its parachor.

Literature contains two references to the sulphur analogue of *cyclo*selenobutane, which was first obtained by von Braun and Trümpler (*Ber.*, 1910, **43**, 545) on condensing tetramethylene iodide with sodium sulphide. Later Grischkevitsch-Trochimovski (*J. Russ. Chem. Soc.*, 1916, **48**, 901) repeated the preparation, confirmed the boiling point, determined the physical constants, and investigated its chemical properties.

Recent papers by Briscoe and Peel (J., 1928, 1741, 2628) on the isolation and description of selenophen furnish data employed in the following comparison of the physical constants of the two pairs of five-membered heterocyclic rings :

Physical pro-perties.	Thiophen (Landolt Börnstein).	Tetrahydro-thiophen (G-T.).	Selenophen (B. & P.).	Tetrahydro-selenophen.
B. p. ...	87°/770 mm.	118—119°	110°/752 mm.	135—136°/770 mm.
D	$1{\cdot}0704_{4°}^{15°}$	$0{\cdot}9607_{4°}^{18°}$	$1{\cdot}5307_{4°}^{19°}$	$1{\cdot}484_{4°}^{18°}$
n	1·5298/18°	1·4871/15°	1·568/15°	1·5510/18°
γ	33·5/0°	—	36·49/15°	40·40/15°

Hydrogenation of the thiophen ring raises the boiling point by about 30°, and a similar difference (35°) is observed between the boiling points of selenophen and its tetrahydro-derivative. These regularities are also supported by the boiling point (113—114°) recorded for selenophen by Mazza and Solazzo (*Rend. Accad. Sci. fis. mat. Napoli*, 1927, **33**, 236).

EXPERIMENTAL.

I. cyclo*Selenobutane* (*Tetrahydroselenophen*) (I).—αδ-Tetramethylene glycol was prepared by reducing ethyl succinate with sodium in anhydrous alcohol, the average yield being *ca.* 50% (compare Müller, *Monatsh.*, 1928, **49**, 27), and this glycol was converted into αδ-tetramethylene dibromide (b. p. 96°/50 mm.) by interaction with dry hydrogen bromide.

Hydrogen selenide, generated by the action of water on 14·5 g. of aluminium selenide, and hydrogen were passed into alcoholic soda made from 6·9 g. of sodium, 250 c.c. of alcohol, and 6 c.c. of water. Colourless sodium selenide separated and when all the hydrogen selenide had been introduced the alcohol was distilled away and cold water was added together with 25 g. of αδ-tetramethylene dibromide (32·5 g. are required by theory, but excess of sodium selenide is desirable).

The mixture was heated at 80° in a current of hydrogen, which prevented oxidation and kept the liquid agitated. After 4 hours the cyclo*selenobutane* was dissolved in carbon tetrachloride, and this extract dried over calcium chloride. Sufficient bromine was then added to convert the selenohydrocarbon into dibromide (yield, 75% of the theoretical). *cyclo*Selenobutane, regenerated by prolonged stirring of the dibromide with water and four times its weight of sodium metabisulphite, was dried over calcium chloride and distilled under reduced pressure. It was noticed that the selenium compound dissolved a considerable amount of sulphur dioxide, which was liberated on heating. The final rectification was effected under ordinary pressure in a stream of carbon dioxide. *cyclo*Selenobutane was thus obtained as a colourless to faintly yellow liquid, b. p. 90—91°/172 mm. and 135—136°/770 mm., $d^{15°}$ 1·484 : densities at other temperatures are given by the expression $D_{4°}^{t°} = 1{\cdot}5060 - 0{\cdot}001354t$. It possessed a very pungent and somewhat unpleasant odour (Found : C, 35·3; H, 6·1; Se, 58·2, 58·35. C_4H_8Se requires C, 35·5; H, 6·0; Se, 58·55%).

Although insoluble in water, the selenohydrocarbon was volatile in steam or in the vapours of alcohol and ether. It was miscible in all proportions with organic solvents. Cold concentrated sulphuric acid gave no coloration, but on warming yellow to red tints were developed. Although *cyclo*selenobutane was only very slowly oxidised in air, hydrogen peroxide promoted oxidation. Aqueous permanganate ruptured the ring, as also did fuming nitric acid, whereas the moderately concentrated acid gave *cyclo*selenobutane 1 : 1-dinitrate.

II. *Additive Compounds of* cyclo*Selenobutane.*—cyclo*Selenobutane mercurichloride*, $C_4H_8Se,HgCl_2$, crystallised in colourless needles

from a warm alcoholic solution of *cyclo*selenobutane and mercuric chloride; it melted to an opaque white liquid at 146° (Found: Cl, 17·2. $C_4H_8Cl_2SeHg$ requires Cl, 17·4%).

cyclo*Selenibutane* 1 : 1-*dichloride* (II) crystallised in colourless plates when chlorine was passed into a carbon tetrachloride solution of *cyclo*selenobutane: it melted at 88—89° (Found: Cl, 34·4. $C_4H_8Cl_2Se$ requires Cl, 34·4%). This dichloride was soluble in chloroform, benzene, or acetone; it dissolved sparingly in alcohol or hot water to a strongly acid solution from which, on cooling, it separated unchanged.

cyclo*Selenibutane* 1 : 1-*dibromide* (II), also prepared by direct addition of its generators, crystallised from benzene, carbon tetrachloride or hot water in lustrous yellow needles, m. p. 92° (Found: C, 16·2; H, 2·7; Br, 54·4; Se, 26·7. $C_4H_8Br_2Se$ requires C, 16·3; H, 2·7; Br, 54·2; Se, 26·8%).

The *perbromide*, $C_4H_8SeBr_2Br_5$, separated in crimson prismatic crystals when concentrated chloroform solutions of bromine and the preceding dibromide were mixed. From dilute solutions it was obtained in large tabular crystals which, although stable in contact with their mother-liquor, decomposed slowly in the air or more quickly on heating, leaving a residue of the dibromide. Acetone also removed five atomic proportions of bromine from this perbromide (Found: Br, 79·7. $C_4H_8Br_7Se$ requires Br, 80·5%).

cyclo*Selenibutane* 1 : 1-*di-iodide* (II) separated in lustrous purplish-black crystals, m. p. 99—100°, when carbon tetrachloride solutions of its generators were mixed (Found: I, 65·4. $C_4H_8I_2Se$ requires I, 65·25%). This di-iodide is only sparingly soluble in organic media and practically insoluble in hot water.

*cyclo*Selenibutane 1 : 1-dihydroxide (VIII) was produced in aqueous solution when the corresponding dibromide was treated with excess of freshly prepared silver oxide. On evaporation of the filtered solution on the water-bath and finally in a vacuum desiccator, colourless highly hygroscopic crystals were obtained. This aqueous solution was neutral to litmus (p_H 6·0—6·2) and addition of aqueous hydrogen halide regenerated the corresponding 1 : 1-dihalide.

cyclo*Selenibutane* 1-*hydroxy*-1-*bromide* (VII). When *cyclo*selenobutane 1 : 1-dibromide was treated with sufficient silver oxide to remove only half its bromine or when equimolecular proportions of 1 : 1-dihydroxide and 1 : 1-dibromide were mixed in aqueous solution, this liquid on concentration over sulphuric acid yielded colourless crystalline *hydroxybromide*, which was freed from any unchanged dibromide by washing with benzene (Found: C, 20·7; H, 3·7; Br, 34·5. C_4H_9OBrSe requires C, 20·7; H, 3·9; Br, 34·4%). This hydroxybromide decomposed slowly on keeping, and on

heating decomposition set in at 99—100°; it was almost insoluble in non-hydrolytic solvents and its aqueous solution was strongly acidic.

cyclo*Selenibutane* 1-*hydroxy*-1-*chloride* (VII), prepared in a similar manner to the foregoing hydroxybromide, was a stable crystalline compound readily soluble in water to a strongly acid solution; it decomposed at 116° (Found: Cl, 18·9. C_4H_9OClSe requires Cl, 18·9%).

cyclo*Selenibutane* 1-*chloroplatinate* (IX) separated slowly in yellow needles from cold dilute aqueous solutions of *cyclo*selenobutane 1 : 1-dichloride and chloroplatinic acid; it decomposed at 230° (Found: Pt, 35·7. $C_4H_8Cl_6SePt$ requires Pt, 35·9%).

Bis-1-*chloro*cyclo*selenibutane* 1-*chloroplatinate* (X). Platinic chloride was added to a warm concentrated solution containing excess of *cyclo*selenobutane 1 : 1-dichloride. After further evaporation and cooling, orange crystals of the complex salt separated which after drying were washed with warm acetone to remove any unchanged dichloride (Found: Pt, 26·3; Cl, 37·3. $C_8H_{16}Cl_8Se_2Pt$ requires Pt, 26·0; Cl, 37·9%). This complex salt melted and decomposed at 179°.

III. *Alkyl and Alkylene Salts of* cyclo*Selenobutane*.—cyclo*Selenibutane* 1-*methiodide* (III). On mixing 27 parts of *cyclo*selenobutane and 27 parts of methyl iodide heat was generated and the *methiodide* was produced, which crystallised from hot water in colourless needles (Found: I, 45·5. $C_5H_{11}ISe$ requires I, 45·8%). On heating in an open tube, this iodide sublimed slowly at about 150°, but in a closed tube it melted at 174°.

1-δ-*Bromobutyl*cyclo*selenibutane* 1-*bromide* (IV). When *cyclo*selenobutane was left in contact with an excess of αδ-tetramethylene dibromide, a colourless glassy compound separated in the course of a few days. After removal of the excess of tetramethylene dibromide and washing with light petroleum, the residue was dissolved in water and the solution evaporated over sulphuric acid. The residual gum crystallised slowly; m. p. 65—66° (Found: Br, 45·3. $C_8H_{16}Br_2Se$ requires Br, 45·5%).

Tetramethylene-αδ-*bis*cyclo*selenibutane* 1 : 1′-*dibromide* (V). A mixture of *cyclo*selenobutane, αδ-tetramethylene dibromide, and water was heated at 90° in a sealed tube with occasional shaking until no more material dissolved in the aqueous layer. This solution was then evaporated over sulphuric acid until the complex *dibromide* separated in colourless prisms, which were dried on porous tile in a vacuum; m. p. 95—96° (Found: Br, 32·9. $C_{12}H_{24}Br_2Se_2$ requires Br, 32·85%).

IV. *Alternative Formations of* cyclo*Selenobutane*.—*Tetramethylene*

αδ-diselenocyanate (XI). Potassium selenocyanate (14·4 g.) and 10·8 g. of αδ-tetramethylene dibromide were heated in acetone solution under reflux for several hours. The filtrate from potassium bromide was evaporated, and water added to the residue; the *diselenocyanate* then separated as a heavy pale yellow oil which slowly solidified (yield, practically quantitative) and was obtained in white flakes, m. p. 40°, by crystallisation from aqueous acetone (Found: C, 27·25; H, 3·2; Se, 59·5. $C_6H_8N_2Se_2$ requires C, 27·0; H, 3·0; Se, 59·45%).

This diselenocyanate, which possessed a penetrating and nauseous odour, decomposed slowly on keeping. Although readily soluble in the ordinary organic media, it was insoluble in water.

cyclo*Tetramethylene diselenide* (cyclo*diselenobutane*) (XII). An alcoholic solution of 5·0 g. of tetramethylene αδ-diselenocyanate was added to alcoholic soda made by dissolving 1·5 g. of sodium in 100 c.c. of alcohol. The yellow liquid was decanted from any precipitate and diluted with 400 c.c. of water, and air bubbled through it for several hours. The *diselenide*, which separated as a yellow powder, sparingly soluble in alcohol or acetone, was washed successively with water and acetone. It dissolved readily in benzene or chloroform and separated from the latter solvent as a yellow gum which subsequently solidified (Found: C, 22·2; H, 3·8; Se, 73·8. $C_4H_8Se_2$ requires C, 22·4; H, 3·8; Se, 73·9%). This diselenide was quite stable on keeping and melted to a yellow liquid at 41—42°; when strongly heated, it decomposed, giving *cyclo*selenobutane, identified by its characteristic odour and by the formation of *cyclo*selenibutane 1 : 1-dibromide.

When the deep red chloroform solution of *cyclo*tetramethylene diselenide (1 mol.) and bromine (2 mols.) was allowed to evaporate at the ordinary temperature, the residue obtained consisted of *cyclo*selenibutane 1 : 1-dibromide (m. p. 92°), black elemental selenium, and tarry material. The dibromide was extracted with carbon tetrachloride. The yield calculated on the resulting dibromide and on selenium recovered was 40% and upwards according to the time of evaporation.

With excess of bromine (4 mols.) an orange precipitate was deposited from the chloroform solution which appeared to be *cyclo*tetramethylene diselenide tetrabromide (XIV) but was so readily decomposed that it could not be analysed. The transformation to *cyclo*selenibutane 1 : 1-dibromide proceeded as before, but the selenium eliminated was obtained as selenium monobromide. The yield of dibromide was not appreciably different from that of the preceding preparation with less bromine.

αδ-Tetramethylenediseleninic acid dinitrate (XIII) separated in

colourless crystals when $\alpha\delta$-tetramethylene diselenocyanate or *cyclo*tetramethylene diselenide was dissolved in warm nitric acid (1 part of concentrated acid : 1 of water) (Found : Se, 38·9. $C_4H_{12}O_{10}N_2Se_2$ requires Se, 39·0%). At 136° this complex acid decomposed with explosive violence and liberation of selenium.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX. [*Received, April 24th*, 1929.]

CXLVII.—*Interaction of Tellurium Tetrachloride and Dimethylaniline.*

By GILBERT T. MORGAN and HENRY BURGESS.

TELLURIUM tetrachloride and dimethylaniline combine in dry ethereal solution to form *bisdimethylaniline tellurium tetrachloride*, $(C_6H_5{\cdot}NMe_2)_2,TeCl_4$, a compound of similar type to the products previously obtained by combination of tellurium tetrabromide and various aromatic bases (Lowy and Dunbrook, *J. Amer. Chem. Soc.*, 1922, **44**, 614).

In the present instance the additive compound is accompanied by a small amount of a substitution product, 4 : 4'-*tetramethyldiaminodiphenyl telluridichloride*, $(NMe_2{\cdot}C_6H_4)_2TeCl_2$, which, however, is more conveniently obtained by digesting the tetrachloride in boiling water, the tellurium migrating into the rings in the para-positions with respect to the two nitrogen atoms. This orientation of tellurium is disclosed by the action of cold nitrous acid, tellurium being eliminated as dioxide and *p*-nitrosodimethylaniline produced.

When reduced directly with alkali metabisulphite, the dichloride furnishes *tetramethyldiaminodiphenyl telluride*, which is also soluble in organic media and is slowly oxidised in the air.

After the conversion of the soluble tetrachloride additive compound into the insoluble dichloride by heating in aqueous solution the concentrated mother-liquor yields on addition of hydrogen chloride a double salt of dimethylaniline hydrochloride and tellurium tetrachloride which crystallises best from alcoholic hydrochloric acid as $(C_6H_5{\cdot}NMe_2,HCl)_3TeCl_4,C_2H_5{\cdot}OH$. This product resembles certain double salts containing tellurium tetrabromide and aromatic bases (Lowy and Dunbrook, *loc. cit.*) and the double halides of tellurium and the alkaloids (Lenher and Titus, *J. Amer. Chem. Soc.*, 1903, **25**, 730).

Preliminary experiments showed that in its interaction with tellurium tetrachloride *N*-methyldiphenylamine resembles dimethylaniline in yielding both an additive compound and a substitution product.

EXPERIMENTAL.

Bisdimethylaniline Tellurium Tetrachloride.—The bright red precipitate, which appeared on addition of 15·2 g. of tellurium tetrachloride, dissolved in 160 c.c. of dry ether, to 21 c.c. of dimethylaniline (3 mols.) in 200 c.c. of the same solvent, rapidly changed to a yellow crystalline solid, which was obtained in practically quantitative yield after washing with ether (Found: C, 37·4; H, 4·6; Cl, 27·8; Te, 24·7. $C_{16}H_{22}N_2Cl_4Te$ requires C, 37·5; H, 4·3; Cl, 27·7; Te, 24·9%).

Bisdimethylaniline tellurium tetrachloride became green at 137° and melted to a blue liquid at 144—145° with elimination of tellurium. It was insoluble in the common organic solvents except acetone and alcohols, which, however, decomposed it. Its bright yellow colour deepened on exposure to light and the substance slowly decomposed in moist air. It formed a colourless hydrochloride stable in dry air but decomposed by alkali with liberation of dimethylaniline.

4 : 4′-*Tetramethyldiaminodiphenyl telluridichloride* was isolated in small amount (0·1 g.) from the concentrated ethereal mother-liquor of the preceding preparation after removal of dimethylaniline with petroleum, but was best prepared by warming 28·5 g. of the foregoing additive compound with 200 c.c. of boiling water for 15 minutes; the initially clear solution then deposited a yellow precipitate, which was extracted with chloroform to separate the organic product from inorganic tellurium compounds. The dichloride which separated from its chloroform solution (yield, 8 g.) crystallised from acetone in well-defined, highly refractive, bright yellow plates or hexagonal prisms which turned blue at 181° and melted to a purple liquid at 188—189° (Found: C, 43·7; H, 4·44; [illegible] Te, 28·9. $C_{16}H_{20}N_2Cl_2Te$ requires C, 43·8; H, 4·6; Cl, 16·2; Te, 29·1%). The dichloride was readily soluble in chloroform or hot benzene, less soluble in acetone and only sparingly soluble in alcohol, ether, or carbon tetrachloride. It dissolved in concentrated sulphuric acid with effervescence, formed a hydrochloride (m. p. 136—137°), and, although insoluble in hot water, dissolved in warm aqueous alkalis to colourless solutions which deposited crystals on cooling. It underwent nitration and its nitro-derivative was reducible to a diazotisable base without elimination of tellurium.

The orientation of tellurium in this dichloride was determined by adding aqueous sodium nitrite (3 mols.) to 1 g. of the dichloride suspended in dilute hydrochloric acid at −5°, the temperature being finally raised to 5°: 0·30 g. of tellurium dioxide and 0·6 g. of *p*-nitrosodimethylaniline were collected, the yields of these products being 80% of the calculated quantities.

4 : 4′-*Tetramethyldiaminodiphenyl telluridi-iodide*,

$(NMe_2 \cdot C_6H_4)_2TeI_2$,

readily obtained by refluxing the dichloride in acetone with a slight excess of sodium iodide, crystallised from chloroform–acetone in lustrous dark red prisms, melting and decomposing at 158—159° with evolution of gas (Found: I, 41·1. $C_{16}H_{20}N_2I_2Te$ requires I, 40·8%).

4 : 4′-*Tetramethyldiaminodiphenyl telluride*, $Te(C_6H_4 \cdot NMe_2)_2$.—Potassium metabisulphite (2 g.) was added to a suspension of 0·8 g. of the dichloride in dilute acetone and after an hour the mixture was extracted with chloroform. Methyl alcohol was added to the dried and concentrated extract; and the solution, filtered from tellurium, was cooled on ice until pale olive-green crystals separated, m. p. 128—130° (Found: C, 52·1, 52·25; H, 6·1, 5·8; Te, 34·6. $C_{16}H_{20}N_2Te$ requires C, 52·2; H, 5·5; Te, 34·7%). This telluride was readily soluble in chloroform, acetone, or benzene, sparingly soluble in alcohol and insoluble in water. It oxidised slowly to a colourless insoluble solid. Even in cold solution it tended to deposit tellurium, and this separation probably caused the variability in colour (orange, orange-red and olive-green) of the various preparations.

Trisdimethylaniline Hydrochloride Tellurium Tetrachloride, $(C_6H_5 \cdot NMe_2,HCl)_3TeCl_4,C_2H_5 \cdot OH$.—In the foregoing preparation of 4 : 4′-tetramethyldiaminodiphenyl telluridichloride the aqueous mother-liquor on concentration yielded a residue, which crystallised from alcoholic hydrochloric acid in greenish-yellow, flattened needles, m. p. 119—121° (Found: C, 38·8, 39·0; H, 4·9, 5·0; Cl, 29·8, 31·35; Te, 15·7, 16·55. $C_{24}H_{36}N_3Cl_7Te,C_2H_5 \cdot OH$ requires C, 39·6; H, 5·4; Cl, 31·5; Te, 16·2%). The alcohol present was identified by conversion into iodoform. This well-defined additive compound, which was readily soluble in water to an acid solution, was less soluble in alcohol. It was hygroscopic and decomposed by aqueous alkalis.

4 : 4′-*Diphenyldimethyldiaminodiphenyl Telluridichloride*,

$(C_6H_5 \cdot NMe \cdot C_6H_4)_2TeCl_2$.

—Tellurium tetrachloride and *N*-methyldiphenylamine in ethereal solution yielded a black viscous oil hardening to an indigo-blue solid (yield, 80%), which was probably an additive compound similar to the first product of the interaction of the tetrachloride and dimethylaniline but not convertible into a dichlorotellurium derivative by the action of water (see p. 1104). The ethereal mother-liquor on concentration left, however, a small amount of viscous solid which after extraction with petroleum to remove *N*-methyldiphenylamine was crystallised repeatedly

from acetone–alcohol (Found: C, 55·6; H, 4·5; Cl, 12·1; Te, 22·6. $C_{26}H_{24}N_2Cl_2Te$ requires C, 55·5; H, 4·3; Cl, 12·6; Te, 22·7%). This dichloride (yield, 5%) separated in well-defined, transparent, primrose-yellow, rhomboidal plates, m. p. 170—172°; it was readily soluble in chloroform or hot acetone and sparingly soluble in alcohol, carbon tetrachloride, or light petroleum. On warming with concentrated sulphuric acid, it developed intense violet to blue colorations, and with nitric acid a deep wine-red tint.

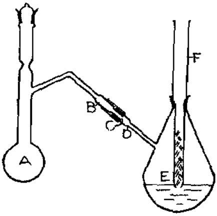
Chemical Research Laboratory,
Teddington, Middlesex. [*Received, April 24th, 1929.*]

NOTES.

The Determination of Available Oxygen by the Bunsen Method.

By Thomas Wallace Parker and Percy Lucock Robinson.

The most recent investigation of the accuracy of the Bunsen method of determining available oxygen by liberation of chlorine appears to indicate that results may be as much as 0·5% low (for potassium permanganate) owing to the reaction between chlorine and water (Rupp, *Z. anal. Chem.*, 1918, **57**, 226). Difficulties attending accepted practice, *viz.*, the tendency for the potassium iodide solution to be drawn back into the reaction flask and the necessity of transferring this solution to another vessel for titration (compare Wagner, *Z. anal. Chem.*, 1903, **42**, 365), have been overcome by using the device shown in the figure.



The apparatus consists of a 50 c.c. flask, A, with a ground-in stopper, sealed by sulphuric acid, and a delivery tube of 8 mm. diameter, widened at B to 10 mm., the end, C, of which is inserted into the especially widened side tube of the absorption flask, rubber being used to complete the joints. The absorption flask, E, is a pear-shaped vessel, 18 cm. high and of 250—300 c.c. capacity, into the neck of which is fitted, by a ground-joint, the tube F, 22 × 2 cm., the rounded bottom of which is pierced with a small hole 8 mm. in diameter. The lower two-thirds of this tube is packed with glass beads. This apparatus is filled to such a height with potassium iodide solution that with the passage of gas the liquid is forced up

the tube 1—1·5 inches above the general level before the pressure is relieved and part of the liquid returns to the main bulk. With such an adjustment there is a continuous interchange of liquid in the bead column, and if for any cause the pressure in the system falls below atmospheric, air passes down the tube into the apparatus.

In carrying out an estimation 20 c.c. of pure concentrated hydrochloric acid were measured into the reaction flask, a fragment of porous pot was added, followed by a small test-tube containing a known weight of pure potassium dichromate, after which the stopper was immediately inserted and $\frac{1}{2}$—$\frac{2}{3}$ of the liquid was gently distilled into the potassium iodide. The absorption flask was then detached, the bead-packed tube removed after being well washed both inside and outside with potassium iodide solution and with water, and the liberated iodine was titrated with thiosulphate solution. Blank experiments with acid alone showed that there was a constant correction of about 0·45 c.c. of 0·04*N*-thiosulphate. The addition of magnesite for the purpose of displacing the last trace of chlorine from the reaction flask was without appreciable effect and the addition of potassium iodide to several lots of diluted residual liquor showed a complete absence of chlorine in all cases. Experiments made in an earlier apparatus, in which the delivery tube was fitted to the neck of the flask by a ground joint, showed that the washing-out of this tube does not raise the result. Lubrication of this ground joint with vaselin or with metaphosphoric acid gave slightly low, or higher but somewhat irregular, results, respectively.

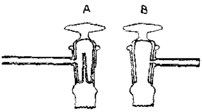
Ten experiments made with 0·1200 g. $\pm$ 0·2 mg. portions of potassium dichromate and titrated to $\pm$ 0·05 c.c. of 0·1*N*-thiosulphate, gave results agreeing among themselves to 1 part in 325 parts, but the mean was about 0·37% low.

In order to find whether the method is susceptible of a high degree of accuracy a second series of experiments was made in which the dichromate was weighed to $\pm$ 0·02 mg. and the chlorine was liberated under slightly less than atmospheric pressure and absorbed at 0°. The thiosulphate was standardised with 0·1*N*-potassium dichromate by means of a weight burette and an approximately 0·04*N*-thiosulphate solution was prepared by the same method. The weight burette was used for the 0·1*N*-thiosulphate in titrating the liberated iodine, the end point being finally reached by use of the weaker solution in a burette, and in this manner results to $\pm$ 0·02 c.c. of 0·1*N*-thiosulphate were obtained. The following figures, the first being the weight of dichromate (g.) and the second the available oxygen %, indicate a concordance of 1 part in 3,250 parts and the mean is 0·18% below the theoretical

alue: 0·24653, 16·281; 0·24319, 16·283; 0·24681, 16·286; 0·12167, 6·285.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. [*Received, February 22nd*, 1929.]

An Improved Calcium Chloride Tube. By DOUGLAS VERNON NELMAR HARDY.

CALCIUM chloride tubes of many different designs have been employed for the absorption of water produced during combustions. Of these, the chief types in common usage are (i) the U-tube with two side-arms, one of which carries a water-trap, and (ii) the U-tube similar to that shown in the diagram but having both stopcocks of design B. The first type may be used many times with the same filling, but has the disadvantage that, while it is waiting to be weighed, rubber caps must be attached. The use of the second type involves frequent replacement of the filling. The advantages of both patterns are possessed by the U-tube shown (as to its upper part) in the diagram, in which stopcock A acts as an efficient water-trap.



—UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, February 26th*, 1929.]

The Volatility and Structures of the Azides and Aliphatic Diazo-compounds. By NEVIL V. SIDGWICK.

THE cyclic structures originally ascribed to these compounds have been generally abandoned in recent years in favour of the open-chain formulæ I and II (as expressed in modern symbols).

$$(I.)\quad R{-}N{=}N{\rightarrow}N \qquad (II.)\quad R_2C{=}N{\rightarrow}N$$

This is due mainly to the work of Angeli, Thiele, and Staudinger, who showed that they give derivatives containing these open chains. The proof that the azoxy-compounds and the *N*-ethers of the oximes have open-chain and not ring structures supported this view. The argument is, however, not very conclusive; it might be urged that the azides and diazo-compounds themselves contain closed rings, and that when these open, since the double link between nitrogen atoms (unlike that between carbons) is normally very strong, they must form unbranched chains.

Lindemann and Thiele (*Ber.*, 1928, **61**, 1529) have shown that the parachors of a series of azides have the values to be expected for the ring structures. But this also is inconclusive, because the difference between the constitutive values calculated for the ring (S·6) and for the open-chain formula I (44·8) is only about 2% of

the total parachor; and though the observed value (mean, 40·3) is nearer to the former than to the latter, it might be maintained that these unusual structures involved a slight modification of the accepted parachor values.

It is to be expected that the volatility of the compounds will throw light on their structures. A co-ordinate link always causes a rise in the b. p., due to the external field of the resulting dipole, as is shown by the b. p.'s of the isomeric pairs $CH_3{\cdot}O{\cdot}NO$, −12°; $CH_3{\cdot}N{\overset{\nearrow O}{\searrow O}}$, 101°: $P(O{\cdot}C_2H_5)_3$, 156°; $C_2H_5(C_2H_5{\cdot}O)_2P{\rightarrow}O$, 198°: $(CH_3)_2N{\cdot}O{\cdot}CH_3$, 30°; $(CH_3)_3N{\rightarrow}O$, >180°. If the azides and the aliphatic diazo-compounds have the ring structures, they should boil at about the same temperatures as the corresponding chlorides or bromides, whereas if they have open-chain structures with the co-ordinate link, their b. p.'s should be much higher, and nearer to those of the nitro-compounds.

In the following tables the published data are collected. The second column gives the pressure in mm. under which the b. p. of the azide or diazo-compound was observed: the values for the halides and nitro-compounds at this pressure have been found by interpolation, or by extrapolation by means of the Ramsay–Young formula; the latter is not very accurate, but the errors should not exceed a few degrees. Compounds whose b. p.'s are recorded at pressures below 10 mm. have been omitted, because of the uncertainty both of the measurements and of the necessary extrapolations.

TABLE I.

Boiling Points of Azides.

	Press. (mm.).	X = N_3.	Cl.	Br.	I.	NO_2.
CH_3X	760	20°	−24°	+ 4·5°	43°	101°
$CH_2Cl{\cdot}CH_2X$	25	45	24	32	68	77
$CH_2Br{\cdot}CH_2X$	20	49	20	33	63	—
$CH_2I{\cdot}CH_2X$	20	68	63	63	—	—
$CH_2{:}CHX$	760	26	−15	+17	—	—
$CH_2{:}CH{\cdot}CH_2X$	760	76	46	71	103	127
$CH_2X{\cdot}CH_2{\cdot}OH$	20	73	50	65	78	105
$CH_2X{\cdot}CH_2{\cdot}OEt$	25	49	19	35	56	72
$CH_2X{\cdot}COCl$	20	50	12	33	55	—
$X{\cdot}CO_2Me$	760	102	71	—	—	—
$X{\cdot}CO_2Et$	760	113	93	—	—	—
$X{\cdot}CH_2{\cdot}CO_2Et$	20	70	52	73	81	101
$CH_3{\cdot}CHX{\cdot}CO_2Et$	16	70	49	59	63	85
$(CH_3)_2CX{\cdot}CO_2Et$	16	71	53	65	—	—
$(CH_3)_2CH{\cdot}CHX{\cdot}CO_2Et$	16	82	74	79	—	94
$CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2X$	20	74	53	67	86	108
C_6H_5X	24	74	37	55	82	106
$C_6H_5{\cdot}CH_2X$	23	108	77	95	—	121
$(p)CH_3{\cdot}C_6H_4X$	15	78	33	48	69	86

TABLE II.

Boiling Points of Aliphatic Diazo-compounds.

	Press. (mm.).	X = N_2.	H, Cl.	H, Br.	H, I.	H, NO_2.
CH_2X	760	—23°	—24°	+4·5°	45°	101°
$CHX{\cdot}CO_2Me$	760	132	130	144	170	203
$CHX{\cdot}CO_2Et$	760	143	145	169	180	216
$CHX{\cdot}CO_2C_5H_{11}$	760	164	190	207	—	—
$CH_3{\cdot}CX{\cdot}CO_2Me$	13	54	38	48	—	—
$CH_3{\cdot}CX{\cdot}CO_2Et$	41	67	72	80	87	112
$CH_3{\cdot}CH_2{\cdot}CX{\cdot}CO_2Et$	11	64	54	64	84	106
$(CH_3)_2CH{\cdot}CH_2{\cdot}CX{\cdot}CO_2Et$	12	72	90	98	—	—
$CH_3{\cdot}CO{\cdot}CX{\cdot}CO_2Et$	12	103	100	103	—	—
$CHX{\cdot}CN$	15	47	27	47	79	—

It will be seen that the b. p.'s of the azides lie near those of the bromides, or between these and the iodides (this was pointed out by Forster and Newman, J., 1910, **97**, 2572, from whose paper several of the values are taken); the b. p.'s of the diazo-compounds lie very near those of the chlorides; those of the nitro-compounds are always much higher. These results seem to indicate that the ring formulæ should be retained for both of these classes of compound.—LINCOLN COLLEGE, OXFORD. [*Received, April 8th*, 1929.]

The Preparation of Quinaldinic Acid. By THOMAS WESTON JOHNS TAYLOR.

THE most convenient way of preparing quinaldinic acid is that of Reissert (*Ber.*, 1905, **38**, 1610) in which the acid is obtained as its copper salt. The tedious operation of removing the copper with hydrogen sulphide can be avoided and the acid obtained much more readily by taking advantage of the low solubility of sodium quinaldinate in cold sodium hydroxide solution.

If the copper salt is boiled with an excess of such a solution (about 2*N*) until all the copper is present as oxide, and the hot solution filtered, sodium quinaldinate crystallises in about 85% yield on cooling. The sodium salt so obtained has the formula $C_9H_6N{\cdot}CO_2Na,1\frac{1}{2}H_2O$, and does not lose its water on standing in a vacuum over calcium chloride (Found : Na, 10·3, 10·4, 10·5. Calc. : Na, 10·4%). The water is lost by heating to 140—150°, or by drying over sulphuric acid in a vacuum (Found: Na, 11·9, 11·7. Calc. : Na, 11·8%). The hydrate of the sodium salt can be purified by recrystallisation from dilute sodium hydroxide solution or from 95% alcohol; in the latter case it first separates as a thick jelly which gradually breaks up into crystals. Rough solubility determinations showed that at room temperature it is about forty times less soluble in 1·5*N*-sodium hydroxide than it is in water.

The acid can be rapidly obtained from the sodium salt by making a paste of the latter with water and adding the theoretical amount of hydrochloric acid. After cooling, the acid can be collected and washed with ice-cold water.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, April 17th*, 1929.]

The Viscosity of Ether at Low Temperatures. By EDM. VAN AUBEL.

THE relation between the fluidity of a normal liquid and the temperature has been shown by the author (*Compt. rend.*, 1921, **173**, 384) to be represented by the formula $\phi = m + n \log (\theta - t)$, where m and n are constants and θ is the critical temperature. This formula was shown to represent satisfactorily the behaviour of several normal liquids above 0°. The recently published measurements of Archibald and Ure (J., 1927, 610) on the viscosities of ether from 0° to −109·8° give the opportunity of testing the validity of the formula at lower temperatures. The following table shows that good agreement is obtained down to −92·2°. The constants used in obtaining the calculated values are: critical temperature of ether $\theta = 193{\cdot}8°$, $m = 4003{\cdot}46$, $n = -1599{\cdot}7$.

Temp.	Fluidity measured.	Fluidity calc.	Diff.	Temp.	Fluidity measured.	Fluidity calc.	Diff.
0°	344·5	344·39	+0·11	−53·9°	174·2	173·89	+0·31
−10·2	308·7	308·75	−0·05	−64·5	144·3	144·79	−0·49
−20·2	275·0	275·5	−0·5	−75·4	115·4	116·08	−0·68
−30·1	243·4	244·09	−0·69	−84·4	93·05	93·22	−0·17
−32·1	238·1	237·9	+0·2	−92·2	74·96	74·01	+0·95
−43·0	206·2	205·17	+1·03				

THE UNIVERSITY, GHENT. [*Received, March 5th*, 1929.]

CXLVIII.—*The Existence of Liquid Racemates.*

By ALAN NEWTON CAMPBELL.

MUCH discussion has centred for many years upon the existence of racemates, as true chemical compounds, in the liquid state and in solution, although the completeness of the dissociation in the gaseous state is well attested by vapour-density determinations. All such work as the present must be undertaken with inactive substances which are known to be true racemates in the solid state, and moreover, it must be known whether the liquid racemates investigated are approaching or receding from their transition points at the temperatures of investigation. It has been shown by Adriani, from freezing-point curves (*Z. physikal. Chem.*, 1900, **33**,

467), and by Findlay and Campbell, from solubility curves (J., 1928, 1770), that solid methyl tartrate is a stable racemate at room temperature, and that its transition point is approached by lowering the temperature. It has also been shown by Findlay and Campbell (*loc. cit.*) that to bring the transition point of a tartaric ester up to the neighbourhood of room temperature it is necessary to introduce some acid group, such as acetyl, propionyl, or benzoyl, in place of the hydroxyl groups. It is therefore probable *a priori* that the liquid esters of racemic acid would be stable racemates, but this does not, of course, preclude the possibility of complete dissociation into the *d*- and *l*-forms on fusion, as is suggested by some authors in the case of other series.

The view, often stated in text-books, that fusion or dissolution of a true racemate is immediately followed by complete dissociation is by no means generally held; indeed, it is obvious on theoretical grounds that the left-hand side of the equilibrium $r \rightleftharpoons d + l$ must be represented by a certain concentration, however small. The statement that in solution the concentration of racemate is negligible rests chiefly upon cryoscopic measurements, but the evidence is not unexceptionable and there are discrepancies. There is one experiment by Byk (*Z. physikal. Chem.*, 1904, **49**, 682; 1908, **61**, 67) which points to the undoubted existence of at least a trace of racemic acid in aqueous solution, and this experiment has been repeated and confirmed by the author.

The state of affairs in a pure liquid racemate is different: there is no medium to exert a dissociating action. It is said that an examination of the physical constants of corresponding active and racemic compounds does not show any marked difference, but this view is not justified, for the results of all investigators do show a difference, although often only very slight.

It is significant that all investigators hitherto have deliberately avoided the use of liquids which were known to be associated. Judging by the experimental data contained in this paper, however, it would seem that in avoiding the associated liquids, they missed the most fruitful field of investigation, for it is just in those cases where the active forms are associated that a most interesting state of affairs exists. Contrary to expectation, the racemic forms are usually less, not more, associated than the active forms. The effect of raising the temperature will be to increase the dissociation of both forms, and hence it would be expected that the physical properties of the two forms should approach one another with rising temperature: this has been found to be the case. Since, however, the rate of increase of dissociation may not be the same in both cases, it may occasionally happen that the order of the

properties may alter, owing to a lag in the dissociation of one form : one such case has been observed.

The literature shows the very conflicting nature of the evidence and of opinions. One fact emerges, however, *viz.*, that the differences in the physical constants are only slight and might be, as is claimed by some, negligible, were it not for the case of ethyl tartrate, investigated by Thole, where the difference between the viscosities of the active and of the racemic form exceeds the experimental error. For the present investigation a series of associated esters of tartaric acid was chosen, *viz.*, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and amyl tartrates and racemates; ethyl diacetyltartrate and methyl dipropionyltartrate were also investigated.

EXPERIMENTAL.

1. *Preparation of the Esters.*—All the active esters, but few of the racemates, had been previously prepared. For the preparation of the latter, the following method was finally adopted. The racemic acid [$(C_4H_6O_6)_2,2H_2O$] (1 mol.) was dehydrated by 6 hours' heating at 110°, finely powdered, and weighed, and the requisite alcohol (4 mols.) was added. The mixture was heated on the water-bath, and saturated with dry hydrogen chloride. (Only by partly esterifying the racemic acid can a large fraction be made to dissolve.) The product was cooled in ice, again saturated, kept over-night, and then distilled under reduced pressure up to 150°. The residue was returned to the esterification flask, and the whole process repeated. Water, alcohol, and hydrogen chloride were removed as before, and the ester was distilled at its appropriate boiling point. The new racemates thus prepared are : n-*Propyl racemate*, m. p. 25° (Found : C, 52·2; H, 7·9. $C_{10}H_{18}O_6$ requires C, 51·5; H, 7·7%); iso*propyl racemate*, m. p. 34° (Found : C, 52·5; H, 7·85%); n-*butyl racemate*, b. p. 185°/12 mm., 320°/765 mm. (Found : C, 55·7; H, 8·65. $C_{12}H_{22}O_6$ requires C, 55·0; H, 8·4%); iso*butyl racemate*, m. p. 58° (Found : C, 55·6; H, 8·5%).

The initial materials in all these preparations were British Drug Houses A.R. racemic acid and A.R. alcohols, with the exception of amyl alcohol, which, being a commercial mixture, gave rise to esters of corresponding isomerides.

2. *Melting Points.*—Although ethyl, *n*-butyl, and amyl racemates were cooled in a freezing mixture to − 16°, and vigorously scratched with glass rods, they could not be induced to crystallise. In the case of *n*-butyl racemate, this is consistent with its physical constants, which indicate that it is very highly dissociated even at room temperature (see below). Thus the eutectic corresponding to the racemate will be far below the freezing point of the active form.

In several cases, notably those of *n*- and *iso*-propyl tartrates, the active ester is liquid at room temperature, whereas the racemic ester is solid. It was thought, in view of this fact and of the high viscosity, that possibly the active esters were merely supercooled liquids. Accordingly, *n*- and *iso*-propyl and amyl tartrates were also cooled to $-16°$. Both the propyl tartrates became very viscous but did not solidify. The amyl tartrate crystallised only partly, doubtless owing to its heterogeneous composition (see p. 1113). Table I gives the melting points, when known, of the active and the inactive esters. The reference (C) denotes that the value is due to the present author.

TABLE I.

Tartrate.	*Dextro.*	*Racemate.*	*Reference.*
Ethyl	17°	Liquid	Franchimont; see Beilstein, Vol. III, p. 513, 1921 edtn.
n-Propyl	Liquid	25° (C)	
*iso*Propyl	Liquid	34 (C)	
n-Butyl	22—22·5	Liquid	Freundler, *Ann. Chim.*, 1894, **3**, 447.
*iso*Butyl	68 (P) 70 (C)	58 (C)	Pictet, *Ber.*, 1881, **14**, 2790.
Amyl	*Liquid*	*Liquid*	
Methyl dipropionyl-	27·5	34·2	Freundler, *Bull. Soc. chim.*, 1894, **11**, 310.
Ethyl diacetyl-	67—68	50·5	McCrae and Patterson, J., 1900, **77**, 1098; Perkin, J., 1887, **51**, 368.

Where the melting point of the inactive form is higher than that of the active, there can be no doubt that the inactive form is, in the solid state, a true racemate. It does not seem reasonable to suppose that, where the racemate has a melting point very much higher than that of the active form, its melting is immediately attended by complete dissociation, but for a more exact knowledge of this it is necessary to investigate fully the form of the freezing-point curve.

3. *Boiling Points.*—The boiling points under reduced pressure and under atmospheric pressure, determined in the usual way, are given in Table II. A short-range Anschütz thermometer was used to minimise the error due to the exposed stem. It is seen that, although in some cases the boiling point of the racemate is lower than that of the active form, it is rarely higher.

4. *Densities and Coefficients of Expansion.*—The densities of all the inactive esters were determined at a number of temperatures. A Sprengel pyknometer holding about 5 c.c. was used in an electrically controlled thermostat, the temperature of which did not vary by more than $\pm 0·05°$. For temperatures of 100° and over, a sulphuric acid bath was used, and here the temperature control was not so good. The coefficients of cubical expansion were also

TABLE II.

Tartrate.			
Ethyl	d	157°/11 mm. (A)	280°/760 mm. (A)
	r	157°/11·5 mm. (A)	281°/765 mm. (C)
n-Propyl	d	171—172°/17 mm. (P)	303°/760 mm. (A)
	d	174°/12 mm. (C)	297°/765 mm. (C)
	r	167°/11 mm. (C)	286°/765 mm. (C)
isoPropyl	d	154°/13 mm. (C)	275°/760 mm. (Pi)
	d		275°/765 mm. (C)
	r	154°/12 mm. (C)	275°/765 mm. (C)
n-Butyl	d	200—203°/18 mm. (F)	320°/765 mm. (C)
	d	186°/14 mm. (C)	
	r	185°/12 mm. (C)	320°/765 mm. (C)
isoButyl	d	197°/23 mm. (Pi)	323—325°/760 mm. (Pi)
	d	195°/13 mm. (C)	311°/768·5 mm. (C)
	r	195°/13 mm. (C)	311°/768·5 mm. (C)
Ethyl diacetyl-	d	193°/30 mm. (C)	291—292°/760 mm. (Pi)
	d		296°/764 mm. (C)
	r	180°/22 mm. (C)	297°/764 mm. (C)

(A) Anschütz, *Ber.*, 1885, **18**, 1399. (F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
(C) Present author. (P) Patterson, J., 1904, **85**, 767.
(Pi) Pictet, *Jahresber.*, 1882, 856.

calculated, as it was thought that these might be less affected by an erroneous determination. The results are in Table III—the figures for the active forms are mostly those of other workers.

An examination of the figures on p. 1116 confirms the statement of Ranken and Taylor (*Proc. Roy. Soc. Edin.*, 1907, **27**, 172) that the racemic form is on the average less dense than the active form: the difference is slight, but persistent. The coefficients of cubical expansion of the active form are almost always higher than those of the racemic form, the mean values of $\alpha \times 10^5$ being:

Ester.	Dextro.	Rac.	Ester.	Dextro.	Rac.
Ethyl	87·5	75	n-Butyl	63·5	67
n-Propyl	86	68	isoButyl	17	18
isoPropyl	88	79·5	Ethyl diacetyl- ...	128	177

The greater densities and coefficients of expansion in the case of active ethyl, n-propyl, and isopropyl tartrates point to a greater association of the active forms. In all cases the coefficient of expansion of the active form increases with rise of temperature, indicating progressive dissociation of the associated molecules.

5. *Viscosities.*—The viscosities of both active and racemic forms were determined at 18°, 40°, and 80°. An ordinary Ostwald viscometer, standardised with water, was used in an electrically controlled thermostat. No special precautions were taken to ensure accuracy in the stop-watch used, beyond comparing it with another in the department; although a slight error might thus affect the absolute value of all these measurements, the relative values for active and

TABLE III.

Ester.		Density. Dextro.		Density. Racemate.	$a \times 10^5$. Range.	$a \times 10^5$. Dext.	$a \times 10^5$. Rac.
Ethyl tartrate	$d^{14°}$	1·2097 (A & Pi)					
	$d^{15°}_{15°}$	1·2097 (P)	$d^{15°}_{15°}$	1·2059 (C)			
	$d^{18°}_{4°}$	1·2112 (C)	$d^{18°}_{4°}$	1·2058 (C)			
	$d^{20°}_{4°}$	1·2036 (W)	$d^{20°}_{4°}$	1·2036 (C)			
	$d^{25°}_{25°}$	1·2019 (P)	$d^{25°}_{20°}$	1·2071 (C)			
	$d^{25°}_{25°}$	1·2151 (C)					
	$d^{40°}_{4°}$	1·1840 (W)	$d^{40°}_{4°}$	1·1876, 1·1873 (C)	20—40°	83	67·5
	$d^{40°}_{4°}$	1·19135 (C)					
	$d^{60°}_{4°}$	1·1642 (W)	$d^{60°}_{4°}$	1·1737 (C)	20—60	84	64
	$d^{60°}_{4°}$	1·1729 (C)					
	$d^{80°}_{4°}$	1·1445 (W)	$d^{80°}_{4°}$	1·1585 (C)	20—80	86·5	65
	$d^{80°}_{4°}$	1·1569 (C)					
	$d^{100°}$	1·1279 (Pi)	$d^{100°}_{0°}$	1·1369 (C)	20—100	84	72·5
	$d^{100°}_{0°}$	1·1274 (C)					
	$d^{131·2°}$	1·0919 (Pa)					
	$d^{131·2°}$	1·0919 (Pa)	$d^{131·2°}$	1·1040	20—131·2	92	90
	$d^{131·2°}_{0°}$	1·0991 (C)					
	$d^{173·8°}_{0°}$	1·0507 (Pa)	$d^{173·8°}_{0°}$	1·0553	20—173·8	95·5	92
	$d^{173·8°}_{0°}$	1·0553 (C)					
n-Propyl tartrate	$d^{17°}$	1·1392 (A & Pi)					
	$d^{18°}_{4°}$	1·1361 (C)	$d^{16°}_{4°}$	1·1360 (C)			
	$d^{20°}_{4°}$	1·1390 (W)	$d^{20°}_{4°}$	1·1256 (C)			
	$d^{40°}_{4°}$	1·1204 (W)	$d^{40°}_{4°}$	1·1159 (C)	20—40	74	41·5
	$d^{40°}_{4°}$	1·1207 (C)					
	$d^{60°}_{4°}$	1·1013 (W)	$d^{60°}_{4°}$	1·0904 (C)	20—60	86	80
	$d^{77·96°}$	1·0819 (Pa)					
	$d^{80°}_{4°}$	1·0819 (C)	$d^{80°}_{4°}$	1·0791	20—80	90	72·5
	$d^{100°}$	1·0590 (Pi)	$d^{100°}$	1·0580	20—100	94	79
*iso*Propyl tartrate	$d^{18°}_{4°}$	1·1274 (C)	$d^{18°}_{4°}$	1·1214 (C)			
	$d^{20°}$	1·1300 (Pi)	$d^{20°}_{4°}$	1·1166 (C)			
	$d^{40°}_{4°}$	1·1057 (C)	$d^{40°}_{4°}$	1·1022 (C)	18—40	89	80
	$d^{80°}_{4°}$	1·0724 (C)	$d^{80°}_{4°}$	1·0743 (C)	18—80	83	71·5
	$d^{100°}$	1·0537 (Pi)	$d^{100°}$	1·0467 (C)	20—100	91	87
n-Butyl tartrate	$d^{15°}$	1·098 (F)	$d^{15°}_{4°}$	1·0890 (C)			
	$d^{18°}_{4°}$	1·0886 (C)	$d^{18°}_{4°}$	1·0879 (C)			
	$d^{40°}_{4°}$	1·0765 (C)	$d^{40°}_{4°}$	1·0741 (C)	18—40	51	57·5
	$d^{80°}_{4°}$	1·0392 (C)	$d^{80°}_{4°}$	1·0382 (C)	18—80	76	77
*iso*Butyl tartrate	$d^{80°}_{4°}$	1·0213 (C)	$d^{80°}_{4°}$	1·0160 (C)	80—100	17	17·8
	$d^{100°}_{4°}$	1·0178 (C)	$d^{100°}_{4°}$	1·0124 (C)			
	$d^{100°}$	1·0145 (Pi)					
Ethyl diacetyl-tartrate	$d^{80°}_{4°}$	1·1065 (C)	$d^{80°}_{4°}$	1·1012 (C)			
	$d^{98·5°}_{4°}$	1·0810 (McC)	$d^{98·5°}_{4°}$	1·0961 (C)	80—98·5	128	177

(A & Pi) Anschütz and Pictet, *Ber.*, 1880, **13**, 1176.
(P) Perkin, J., 1887, **51**, 363. (W) Winther, *Z. physikal. Chem.*, 1902, **41**, 174.
(Pi) Pictet, *Jahr.*, 1882, 856. (Pa) Patterson, J., 1908, **93**, 1852.
(F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
(McC) McCrae and Patterson, J., 1900, **77**, 1098. (C) Present author.

racemic compounds are not affected. The results are in Table IV. Thole (J., 1910, **97**, 1249) found 1·457 for ethyl tartrate and 1·360 for the racemate at 25°.

TABLE IV.

Ester.	18°. *d.*	18°. *r.*	40°. *d.*	40°. *r.*	80°. *d.*	80°. *r.*
Ethyl	3·7996	2·5196	0·4479	0·3499	0·0571	0·0536
n-Propyl	2·0760	1·4861	0·3587	0·2965	0·0524	0·0461
*iso*Propyl	7·6161	5·8243	0·5716	0·6150	0·0643	0·0647
n-Butyl	1·0587	0·9455	0·2532	0·2475	0·0455	0·0445
Amyl	1·9851	1·8654	0·4093	0·3326	0·0586	0·0527
Methyl dipropionyl-			0·3411	0·3355		
Ethyl diacetyl-					0·0656	0·0460
*iso*Butyl					0·0640	0·0695

The marked difference in the viscosities is noteworthy; with one exception, that of the active form is, in agreement with Ranken and Taylor (*loc. cit.*), Aguirreche (*Anal. Fis. Quim.*, 1925, **23**, 409), and Thole (*loc. cit.*), higher than that of the racemic form, but *iso*propyl tartrate at 40° showed the reverse behaviour, and this was confirmed with several fresh preparations. As the temperature rises the difference in the viscosities decreases, becoming in some cases almost zero; thus, in the case of *iso*propyl tartrate at 80° we may perhaps conclude that the dissociation of the racemate is complete. The following ratios of $\eta_{\text{tartrate}}/\eta_{\text{racemate}}$ and also the temperature coefficients $(d\eta/dt)/\eta_{18°}$ illustrate these points.

Ester.	18°. Ratio.	40°. Ratio.	40°. $(d\eta/dt)/\eta_{18°}$. *d.*	40°. $(d\eta/dt)/\eta_{18°}$. *r.*	80°. Ratio.	80°. $(d\eta/dt)/\eta_{18°}$. *d.*	80°. $(d\eta/dt)/\eta_{18°}$. *r.*
Ethyl	1·51	1·28	0·0401	0·0393	1·07	0·0159	0·0158
n-Propyl	1·40	1·21	0·0378	0·0363	1·13	0·0157	0·0156
*iso*Propyl	1·30	0·93	0·0420	0·0407	1·00	0·016	0·159
n-Butyl	1·12	1·02	0·0345	0·0336	1·02	0·0153	0·0154
Amyl	1·065	1·23	0·036	0·0374	1·12	0·0157	0·0156
Methyl dipropionyl-		1·01					
Ethyl diacetyl-					1·42		
*iso*Butyl					1·29		

Thole's figures (*loc. cit.*) for ethyl tartrate give ratio = 1·07, and $(d\eta/dt)/\eta_{18°}$ = 0·088 for the tartrate and 0·066 for the racemate.

The temperature coefficients of the active forms are greater than those of the racemic forms, but all approach the value 0·016 at 80°. In view of such striking evidence as the above, it can hardly be denied that there must at least be a great difference in the degrees of association of the two forms. The greater viscosity of the active form points to a greater association of that form.

6. *Refractivities and Dispersions.*—The refractive indices for the hydrogen *C* and *F* lines were determined in a Zeiss Pulfrich refractometer, through which water at 18° was circulated. The instrument

was adjusted in the usual manner, and standardised with water. The calculated molecular refraction assumes the presence of two hydroxylic, two ketonic, and two ethereal oxygen atoms. The results, given in Table V, show slight but distinct differences, as elsewhere, the active form having usually the greater refractive index, and the inactive the greater dispersion.

TABLE V.

Ester.	Ethyl.	*n*-Propyl.	*iso*Propyl.	*n*-Butyl.	Amyl.
d n_C ………………	1·4466	1·4447	1·4385	1·4455	1·4440
d n_F ………………	1·4556	1·4532	1·4467	1·4544	1·4544
r n_C ………………	1·4453	1·4413	1·4374	1·4451	1·4452
r n_F ………………	1·4546	1·4523	1·4461	1·4568	1·4580
d $[R_L]_C$ ……………	45·51	54·79	54·41	64·12	72·85
d $[R_L]_F$ ……………	46·20	55·69	55·42	65·23	74·33
r $[R_L]_C$ ……………	45·48	54·43	54·71	64·12	72·98
r $[R_L]_F$ ……………	46·43	55·63	55·65	65·75	74·81
Calc. $[R_L]_C$ ………	45·29	54·49	54·49	63·68	72·87
Calc. $[R_L]_F$ ………	45·97	55·31	55·30	64·74	74·33
d; $[R_L]_F - [R_L]_C$ …	0·69	0·90	1·01	1·11	1·48
r; $[R_L]_F - [R_L]_C$ …	0·946	1·205	0·94	1·63	1·83

7. *Surface Tension.*—Following on the work of Mitchell and Smith (J., 1913, **103**, 489), the surface tension, molecular surface energy, and temperature coefficient of the latter were determined. The stalagmometer method was used, the instrument being standardised with water. The high viscosity prevented its use at 18°. For the same reason, the smallest size of Traube stalagmometer, having a drop number of about 21·5 at room temperature, was used. The simple ratio of the drop weights was used, no corrections being applied. The reason for this was principally that only comparative figures were required, and, secondly, that the order of reproducibility of the surface tensions of these viscous esters is not so high as with, *e.g.*, water or benzene. The results are in Table VI.

TABLE VI.

	γ.			$\gamma(Mv)^{\frac{2}{3}}$.		$k = d[\gamma(Mv)^{\frac{2}{3}}]/dt$.	
Ester.	*d*.	*r*.	*t*.	*d*.	*r*.	*d*.	*r*.
Ethyl	31·78	30·71	40°	986	955		
	31·37	30·28	80	993	958	+0·175	+0·075
n-Propyl	28·96	27·32	40	1018	993		
	27·10	25·32	80	977	914	—1·02	—1·98
*iso*Propyl	28·40	26·58	40	1000	946		
	26·27	25·70	80	952	930	—1·425	—0·40
n-Butyl	28·73	28·36	40	1120	1108		
	27·20	26·17	80	1086	1045	—0·85	—1·575
*iso*Butyl	24·17	24·79	80	976	1004		
Amyl	26·90	26·16	40	1143	1120		
	24·90	23·70	80	1085	1035	—1·45	—2·125
Ethyl diacetyl-	27·47	27·57	80	1125	1133		

The most striking observation is that the values of k are, with one exception, greater for the r than for the d form; in other words, the association of the active form is greater than that of the racemic, a surprising result on the basis of the assumption of simple association of oppositely active molecules to single racemate molecules. It is also noteworthy that the only case in which k is smaller for the r than for the d form, and therefore the association of the racemate is greater than that of the active form, is also the only case (at 40°) where the viscosity of the racemate is greater than that of the active form.

8. *Specific Rotations.*—An examination of the preceding physical constants shows that those of the active and of the racemic forms tend to become identical with rising temperature. The most obvious and probable explanation of this is that both forms are dissociating into single molecules. Another explanation is conceivable, however, *viz.*, that with rising temperature a reversible racemisation of the active form takes place. This hypothesis is disposed of by an examination of the specific rotations of the active forms at different temperatures (Table VII). In the case of most of the esters this had already been done by previous workers, but

TABLE VII.

Ester.	Temp.	$[\alpha]_D$.	Ester.	Temp.	$[\alpha]_D$.
Ethyl	14°	7·07° (S)	*n*-Propyl	14°	11·7° (C)
tartrate	17·8	7·64 (Pa)	tartrate	17	12·39 (Pa)
	20	7·659 (Pi)		18	12·09 (A & Pi)
	20	7·45 (Wa)		20	12·44 (Pi)
	20	7·48 (Wi)		20	12·00 (Wi)
	35·3	9·39 (Pa)		98·5	17·28 (Pa)
	92·9	13·28 (Pa)		100	17·11 (Pi)
	100	13·29 (Pi)	*iso*Propyl	14	15·70 (C)
	143	14·75 (Pa)	tartrate	20	14·886 (Pi)
	175	14·99 (Pa)		100	18·821 (Pi)
*iso*Butyl	100	19·87 (Pi)	*n*-Butyl	*14	10·09 (C)
tartrate		(homogeneous)	tartrate	19	10·3 (F)
	14	11·8 (G & F)		80	13·77 (C)
		(c = 1·025 in alcohol)	Ethyl	56·8	4·37 (McC & P)
		13·6 (C)	diacetyl-	100	6·30
		(c = 37·0 in alcohol)	tartrate		

* The rotation of *n*-butyl tartrate appears to be affected by a species of mutarotation, for after several months' keeping the rotation had decreased to +8·94°.

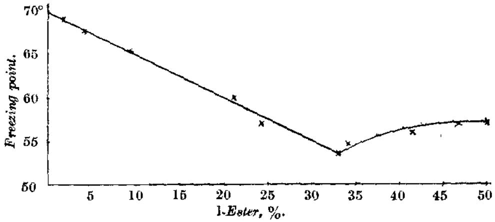
(Pa) Patterson, J., 1908, **93**, 1852; 1904, **85**, 767.
(Pi) Pictet, *Jahresber.*, 1882, 856.
(Wa) Walden, *Ber.*, 1905, **38**, 399.
(Wi) Winther, *Z. physikal. Chem.*, 1907, **60**, 576.
(A & Pi) Anschütz and Pictet, *loc. cit.*
(F) Freundler, *Ann. Chim.*, 1894, **3**, 447.
(G & F) Guye and Fayollet, *Bull. Soc. chim.*, 1895, **13**, 207.
(McC & P) McCrae and Patterson, *J.*, 1900, **77**, 1098.

a few new determinations are added. From these figures it is evident that the rotation always increases with rise of temperature, and therefore the hypothesis of racemisation is untenable.

9. *Freezing-point Curve of* iso*Butyl Tartrate.*—*iso*Butyl tartrate breaks the series of liquid esters, for it is solid up to 70°, and the racemate up to 58°. It was thought, however, that some light might be thrown on the degree of dissociation of the racemate from the form of the freezing-point curve (compare Roozeboom, Adriani, Findlay and Hickmans, Findlay and Campbell, *locc. cit.*). As these tartaric esters all tend markedly to remain superfused, the temperature was allowed to fall slightly below the expected freezing point,

FIG. 1.

Freezing-point curve of mixtures of isobutyl d- *and* l-*tartrates.*



and a crystal of the phase separating was then added. In this way the following data were obtained, from which Fig. 1 is plotted.

l-Ester, %	0·00	1·57	4·19	9·43	21·26	24·24
F. p.	69·8°	69·0°	67·7°	65·2°	60·0°	57·0°
l-Ester, %	32·8	34·10	41·44	46·52	48·64	50·00
F. p.	53·4° (*eutectic*)	54·5°	55·9°	56·8°	57·0°	57·2°

From the form of the curve, the range of stability of the racemate appears to be much less than that of the racemate of methyl tartrate investigated by Adriani (*loc. cit.*). The flatness of the intermediate portion of the curve indicates a high degree of dissociation of the racemate in the molten state.

10. *Solubility Curves of* iso*Butyl Tartrate.*—It has been shown by Roozeboom that a study of the solubility of the active, inactive, and mixed active and inactive phases will decide whether the solid inactive form is a true racemate or simply a *dl*-conglomerate. Accordingly, such measurements were carried out on *iso*butyl tartrate. In the case of the mixed solid phase, it was necessary to analyse the solution polarimetrically to determine the relative

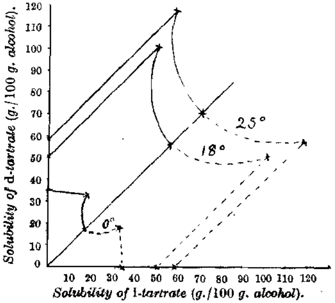
proportions of active and inactive ester. The author's value for the specific rotation of *iso*butyl tartrate in alcoholic solution was used rather than that of Guye and Fayollet (see Table VII) since it is more nearly related to saturated solutions. The following values were obtained, and they are plotted in Fig. 2.

	Solubility (g./100 g. alcohol).		
Solid phase.	0°.	18°.	25°.
d	35·0	50·7	58·4
r	34·9 *	56·5 *	71·5 *
d + *r*	33·75 *d* 18·35 *l*	101·85 *d* 51·15 *l*	117·75 *d* 58·25 *l*

* Total, *d* + *l*.

Fig. 2.

Solubilities of iso*butyl* d- *and* l-*tartrates.*



The total solubility is always increased by addition of the active form to the inactive, *i.e.*, the liquid phase becomes active. At all the above temperatures, therefore, the solid inactive form is a solid racemate. It will be observed that the length of the intermediate portion of the curve is decreasing with falling temperature, and at 0° is comparatively small. Therefore, at temperatures somewhat below 0°, the solid phase will pass from true racemate to *dl*-conglomerate. The point of significance for this work, however, is that at temperatures above 0°, the stable solid phase is always a true racemate, and it might therefore be expected that differences might exist in the physical constants of the two forms. The above state of affairs has also been shown to exist in the case of methyl tartrate (Findlay and Campbell, *loc. cit.*) and therefore, by analogy, in that of all the simple tartaric esters.

11. *Byk's Experiments.*—Although not directly concerned with the matter of this paper, the experiments of Byk (*loc. cit.*) on the existence of racemic molecules in solution were thought of sufficient interest to be repeated. That author prepared two specimens of alkaline Fehling solution, one made up with tartaric acid, and the other with the equivalent amount of racemic acid; the latter was bluer and the former greener, and this difference was still very marked at 100-fold dilution, and still detectable at 250. On repeating this experiment, the present author noticed at first a decided difference, but this seemed rather to consist in a greater opacity of the racemic solution than in a difference of tint. On dilution 50 times the relative difference in tint became more marked, and the racemic solution was then distinctly bluer.

The absorption spectra of the original solutions were then determined with a Hilger constant-deviation spectrometer. The visible spectrum extended from $\lambda = 7610$ Å. to $\lambda = 4255$ Å. There was no absorption in the violet. The following table shows the wave-lengths of the absorption bands for given layer thicknesses for the two solutions:

Tartrate.		Racemate.	
λ.	Thickness, mm.	λ.	Thickness, mm.
7610—6180	29	7610—5438	40
7610—6640	15	7610—6500	20
7610—7195	8	7610—6800	10
No band	4	7610—7550	5

The λ-log thickness plot gives two closely parallel graphs, the difference being probably due to a slight difference in concentration. There is therefore no evidence here of the existence of racemic molecules. The head of the band lies in the infra-red.

Another interesting observation is that when both the tartrate and racemate Fehling solutions were kept for several weeks, cuprous oxide was deposited from the former solution, but not from the latter. Now, according to Byk (*loc. cit.*), tartrate Fehling is photochemically active: as the racemic molecules cannot be present to any great extent, the effect must be an anticatalytic one.

Conclusion.

From an examination of the physical constants, the conclusion is irresistible that in the case of the liquid esters of tartaric acid there is a marked difference in the chemical nature of the active and inactive forms.

As the series of esters is ascended from the ethyl to the amyl members, the difference in the degree of association decreases, at

room temperature, so that amyl tartrate appears to be but little more associated than its racemic form. As the temperature rises, the active form dissociates more than the racemic form, so that *n*-butyl racemate has become identical with its active form. At the same time, it must be supposed that sometimes the racemate (which must also be associated to some extent) dissociates at a different rate from the active form, for, *e.g.*, the order of viscosities of *iso*-propyl *d*- and *r*-tartrate is reversed at 40°, whereas the viscosities of the amyl esters, almost identical at 18°, show a considerable difference at 40°. At 80°, the constants are still closer.

UNIVERSITY OF ABERDEEN. [*Received, March 15th, 1929.*]

CXLIX.—*Effect of the Addition of Hydrogen and Water on the Radiation emitted from the Carbon Monoxide Flame.*

By WILLIAM EDWARD GARNER and F. ROFFEY.

THE flame of carbon monoxide and oxygen emits the major part of its radiation in two bands with maxima at wave-lengths 2·8 and 4·4μ, which correspond to the infra-red emission and absorption bands of carbon dioxide gas. On account of this correspondence, it is concluded that the emitters of the infra-red radiation from the flame are molecules of carbon dioxide (compare Garner and Johnson, *Phil. Mag.*, 1927, **3**, 97; *J.*, 1928, 281; Johnson, *Phil. Mag.*, 1928, **5**, 301). The spectrum of the flame in the ultra-violet and visible regions consists of a continuous band ranging from 5500 to 2300 Å., on which are superimposed carbon monoxide bands, the wave-lengths of which have been measured by A. Fowler ("Flame and Combustion in Gases," Bone and Townend, p. 331).

The addition of hydrogen or water to the flame of carbon monoxide causes a diminution in the intensity of emission of radiation over the whole spectrum. The total radiation is reduced to one-eighth on the addition of 2% of hydrogen (see below). Weston (*Proc. Roy. Soc.*, 1925, *A*, **109**, 177, 523) has shown that the visible and ultra-violet spectrum of the carbon monoxide flame practically disappears on the addition of 50% of hydrogen, the place of the carbon monoxide spectrum being taken by the hydroxyl bands in the ultra-violet. Experiments by Johnson (*loc. cit.*) have shown that the emission at both 2·8 and 4·4μ is diminished on addition of water vapour.

These changes in the character and intensity of the radiation from the carbon monoxide flame on the addition of hydrogen and water are of importance for the study of the catalytic effect on the speed

of flame discovered by Dixon (*Phil. Trans.*, 1884, **175**, *A*, 617), which was explained by him as due to the action of steam :

$$(1)\ CO + H_2O \longrightarrow CO_2 + H_2$$
$$(2)\ 2H_2 + O_2 \longrightarrow 2H_2O, \text{ etc.}$$

Bone, from the above changes in the ultra-violet spectrum and from the fact that the gas dried for two years over phosphoric oxide can still give rise to flame, concludes that two independent reactions occur in this flame : (1) a dry reaction, and (2) a reaction catalysed by steam.

The mechanism of catalysis suggested by Dixon is based on a chemical explanation of the catalytic effect. There is, however, an alternative interpretation of the increased speed of flame caused by the addition of hydrogen or water vapour, *viz.*, that it is due to physical processes, *e.g.*, to collisions of the second kind. The fact that the radiation from the carbon dioxide molecules produced in the flame is reduced on the addition of hydrogen is suggestive in this connexion. Energy which is emitted as radiation in the absence of hydrogen is retained within the reacting gases when it is present, and this energy must be available in one form or another for facilitating the chemical change. Thus, a physical explanation of the phenomenon is not ruled out by the experimental evidence. A typical mechanism, illustrating a catalytic effect due to collisions of the second kind, is shown in equations (3)—(6) :

$$(3)\ 2CO + O_2 \longrightarrow 2CO_2'$$
$$(4)\ CO_2' \longrightarrow CO_2 + h\nu$$
$$(5)\ CO_2' + X \longrightarrow CO_2 + X'$$
$$(6)\ X' + O_2 \longrightarrow X + O_2', \text{ etc.},$$

which illustrate the formation of activated molecules of carbon dioxide by the chemical change (3), their deactivation by emission of radiation (4) and by collision with a third substance X (5), and the transference of the energy from X′ to one of the reactants (6). This chain mechanism provides an explanation of the decrease in radiation on addition of hydrogen, and is also in agreement with the fact that the addition of substances which do not increase the speed of the reaction, *e.g.*, nitrogen, oxygen, carbon monoxide, carbon dioxide, etc., does not decrease the emission of radiation.

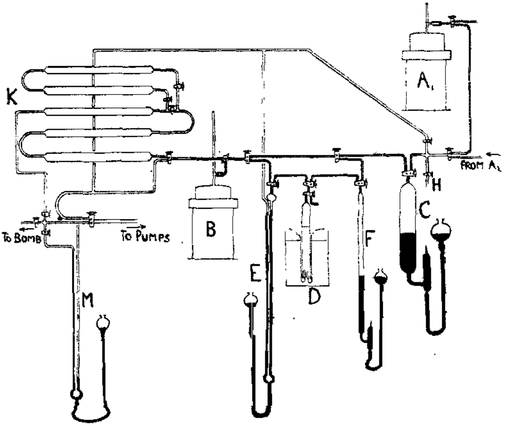
It is not improbable that both the chemical and the physical type of catalytic effect are present in flames. In order to determine the extent to which these two types of effect occur in the carbon monoxide flame, the following investigation was undertaken.

EXPERIMENTAL.

The experimental method employed has been described in previous communications (*locc. cit.*), and only a broad outline of the methods

used is now given. The gaseous mixtures, enclosed in a cylindrical phosphor-bronze bomb, are ignited at one end of the bomb by the fusion of thin iron wire (this may be replaced by a thin platinum wire), a 12- or 24-volt battery being used as a source of current. The radiation from the flame emerges through a fluorite window in the bomb and is measured by a Moll thermopile and a Downing galvanometer. Fig. 1 shows the arrangement for drying and storing the gases. Carbon monoxide was prepared from pure formic acid

Fig. 1.



and sulphuric acid, and oxygen by heating pure permanganate. The hydrogen was added in the form of electrolytic gas.

The carbon monoxide was stored in glass vessels over water in the majority of the experiments recorded here (A_2, Fig. 1), it having been found that a metal gas-holder evolved sufficient hydrogen to the gas to vitiate the results for low hydrogen concentrations. The oxygen after drying was stored over mercury (A_1). The dried gases were mixed in the proportion $2CO : 1O_2$, and stored in a gas holder over mercury (B). The gases were further dried by standing for one hour over phosphoric oxide, which had not been distilled in oxygen before use, but was practically free from phosphorous oxide. The pentoxide gave no precipitate with the mercuric chloride test, but gave a positive test for trioxide by the silver nitrate method.

A lengthening of the period of contact of the gases over pentoxide did not affect the radiation emitted or the speed of flame. Contact with pentoxide over-night or for several days had no effect. The water present in the walls of the bomb was troublesome to remove, especially after explosions of mixtures containing hydrogen. Drying for one hour with a Hyvac pump was not sufficient to remove this water, but, by using a Ley bolt condensation pump in conjunction with the Hyvac pump, and pumping for one hour, steady and reproducible values for the radiation and speed of flame were obtained. Further evacuation did not alter the values. After experiments with flames containing large quantities of hydrogen, a longer period of evacuation must be employed before carrying out experiments on hydrogen-free mixtures. Although it is unlikely that the whole of the water vapour in the walls of the bomb was removed by this treatment, the water escaping from the walls into the gases during an experiment of 5—10 minutes' duration must be very small. The percentage of hydrogen present in the gases after this treatment could not be very large, for 0·005% of hydrogen, when added to these gases, practically doubled the speed of flame, and reduced the radiation by 15%. Further experiments are now being carried out in a rustless steel bomb, which can be heated in a vacuum at 300—400°, and this will make it possible to carry the investigation into the region of smaller hydrogen concentration. The method of introducing electrolytic gas is shown in Fig. 1, which is self-explanatory.

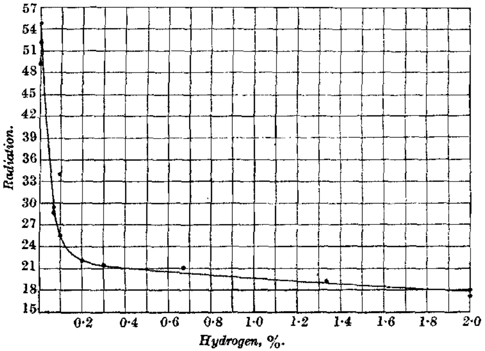
The speed of flame movement was measured simultaneously with measurements of radiation by the method described in previous papers. The only modification of note was the replacement of the falling-plate camera by a revolving drum carrying negative paper. This made it possible to measure the speeds of movement of flame with greater accuracy. Considerable experimental difficulties were experienced before the Einthoven galvanometer could be made to yield trustworthy results. The trouble appeared to be a leak of alternating current to the instrument, and was minimised by insulating all of the recording apparatus and by earthing the field magnets through a resistance.

Two bombs were used, both of 2·5 cm. internal diameter, one 40 and the other 80 cm. long. The longer bomb was provided with three pairs of insulated electrodes mounted at intervals of 10, 32·5, and 73·5 cm., respectively, from the firing plug, itself placed 3—4 cm. from the valve end of the bomb. The platinum wires of the insulated electrodes penetrated 3 mm. into the bomb, and the tips of each pair were separated by 2·5 mm. These were used in the measurement of speed of flame.

The deflexions of the Downing galvanometer were sometimes observed visually and sometimes photographically. The error in the visual readings was about 2 mm. on a deflexion of 40 cm.

Preliminary Series of Experiments.—In this series, a metal gasholder was used for storing carbon monoxide, and hence the explosive mixture may have contained small amounts of hydrogen. The small bomb was used, and the experimental arrangement was practically that of the preceding paper. A Hyvac pump was used for evacuation. No speeds of flame were measured. The results are shown graphically in Fig. 2, each point shown being the mean

FIG. 2.



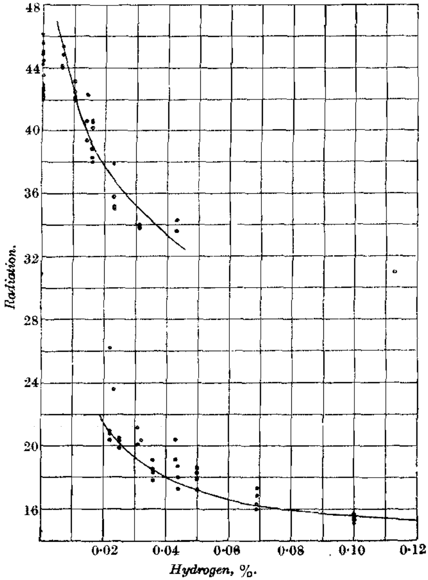
of a number (4—8) of readings. The fall in radiation on addition of hydrogen is very marked.

Series with the Long Bomb: Speed and Radiation Measurements.—The individual experimental results for this series are all shown in Figs. 3 and 4. The galvanometer deflexions are plotted against the % of hydrogen added in Fig. 3, and against 1/log speed in Fig. 4. For the small percentages of hydrogen (less than 0·02%), the deflexions were not proportional to the radiation received by the thermopile, and this was found subsequently to be the cause of the apparently irregular results with the dried gas mixture. For the lowest speeds of flame, with a galvanometer period of 2 seconds, it is necessary to record the deflexions by a photographic method, and to measure the area below the curve so obtained.

The measurements of the velocity of movement of flame were

usually made between electrodes 63·5 cm. apart. The time taken for the flame to travel between these two electrodes could be measured accurately. In a few cases, the speed was also measured between electrodes 1 and 2 which were 22·8 cm. apart. At this distance, there was sometimes interference between the deflexions

FIG. 3.



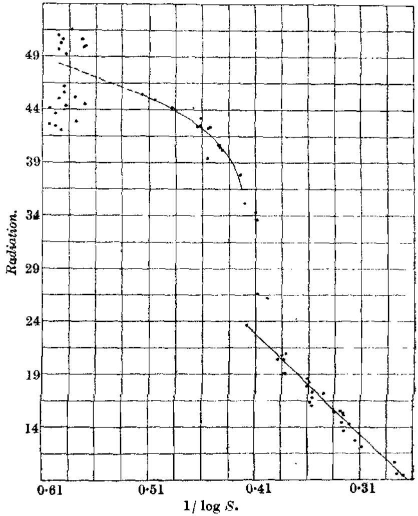
caused by the flame passing the two pairs of electrodes. The trustworthy results obtained are given below :

Radiation emitted		44·3	42·6	41·3	39·9	23·4	19·0	14·7
Mean speed (cm./sec.) between electrodes.	1—2.	49	120	128	180	256	319	1100
	1—3.	61	147	149	244	240	423	1140

The average speed of flame between the first and the second electrode is usually somewhat smaller than that between the first

and the third. There is, however, no very marked increase in the speed of the flame as it moves along the bomb. This was shown previously to be the case for the smaller bomb (compare Garner and Johnson, J., 1928, 290). The dry mixture without hydrogen is exceptional; for this mixture the speed between the first and second electrodes is greater than that between the second and third. The speeds recorded subsequently are in all cases the average speeds between electrodes 1 and 3, placed 63·5 cm. apart.

FIG. 4.



The main feature of Fig. 3 is the step on the curve; the region between 0·02 and 0·04% of hydrogen is an unstable region in which samples of one and the same mixture give deflexions which lie on one or other of two definite curves. One or two intermediate points were found. In this region, there is a sudden change in the nature of the Einthoven records (see later). The results for quantities of hydrogen greater than 0·10% are not included in Fig. 3; the mean values for all concentrations of hydrogen are, however, given in

Table I, where the deflexion is a measure of the radiation, and *u* and *l* refer to the upper and lower curves, respectively.

The step also occurs at the same percentages of hydrogen in Fig. 4. The logarithmic scale is employed for the speeds of flame movement, partly for convenience in plotting, and partly for theoretical reasons. The composition–log speed curve shows evidence of the existence of a slight step which is, however, nearly masked by the experimental error. In a number of experiments (see below) where the emission of radiation varied considerably, nearly identical speeds of flame were obtained. Thus it is improbable that the decrease in radiation at the step at 0·02—0·04% hydrogen is due to changes in the speed of flame movement.

Expt. No.	H_2, %.	Radiation (cm.).	Speed (cm./sec.).
263	0·023	37·9	227
264	,,	23·6	243
268	0·043	33·6	287
269	,,	26·6	282

TABLE I.

Radiation and Speeds of Flame.

H_2, %.	Deflexion (cm.). *u*.	*l*.	Mean speed (cm./sec.). *u*.	*l*.	H_2, %.	Deflexion (cm.). *u*.	*l*.	Mean speed (cm./sec.). *u*.	*l*.
0·006	44·7	—	101	—	0·05	—	18·0	—	597
0·01	42·5	—	150	—	0·07	—	16·4	—	649
0·016	40·6	—	175	—	0·10	—	15·4	—	1150
0·023	*36·0 and*	*22·4*	*237 and*	*409*	*0·20*	—	*14·1*	—	*1210*
0·025	32·0 ,,	20·3	—	—	0·30	—	13·0	—	—
0·031	33·9 ,,	21·0	—	—	0·50	—	10·3	—	1883
0·036	—	18·4	—	—	0·67	—	9·8	—	4070
0·043	33·9 ,,	19·8	281 ,,	394	1·00	—	8·8	—	—
0·044	—	17·4	—	—	2·00	—	8·9	—	4740

The order of the above experiments was haphazard. Measurements with mixtures with the higher percentages of hydrogen sometimes preceded and sometimes followed those with the lower percentages. The points lying between the two curves are not included in the means. The speed of flame for the dried gases containing no hydrogen was 45—55 cm./sec. Lower speeds of flame have since been obtained by Mr. D. H. Hall with another apparatus.*

Effects of Small Quantities of Hydrogen on the Radiation Emitted.—The upper region of curves (Figs. 3 and 4) was further investigated. In these curves, the deflexions given for the gases containing

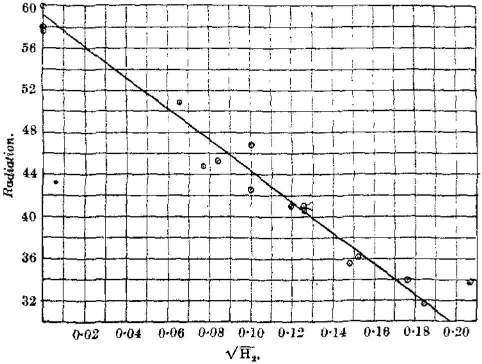
* With a new experimental arrangement, the following limiting speeds were obtained for the dried gas mixture:

Dried with commercial P_4O_{10}, 39—41 cm./sec.
,, ,, distilled P_4O_{10}, 35—37 ,,

The difference is not so great as that which occurs on changing an old phosphoric oxide tube attached to the pump for a new tube.

percentages of hydrogen up to 0·01% require correction on account of departure of the galvanometer deflexions from ballisticity. The necessary correction was obtained by using a photographic method of recording the deflexions. A very accurate clock motor was lent to us by Professor Buckmaster for this purpose. The records taken on this instrument were time-marked in fifths of a second. The areas under the curves, which are proportional to the radiation falling on the thermopile, were measured, and by plotting these areas against the maximum deflexions, a correction curve was obtained. This was used to correct the points in Figs. 3 and 4.

Fig. 5.



The corrected results, together with the new figures, are given in Fig. 5, the radiation being plotted against $\sqrt{H_2}$.

The corrected values for the radiation are also employed in Fig. 6, where are given the radiation–log speed curves for small percentages of hydrogen (I) and of water vapour (II).

In Table II are given the results of a typical series of experiments in the region 0·00—0·016% of hydrogen, determined by the above method; the value shown against the bracket in each case is the mean of the bracketed values.

Effect of Water Vapour on the Radiation and Speed of Explosion of Carbon Monoxide and Oxygen.—Water vapour, which has a similar effect to hydrogen on the phenomena of the carbon monoxide flame, was introduced into the evacuated bomb from a small bulb containing water at a constant temperature lower than that of the

Fig. 6.

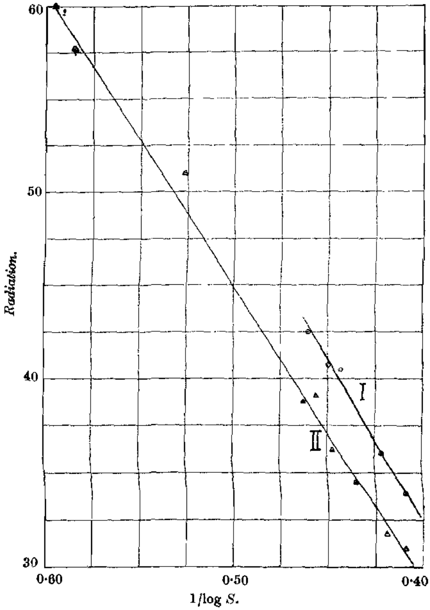
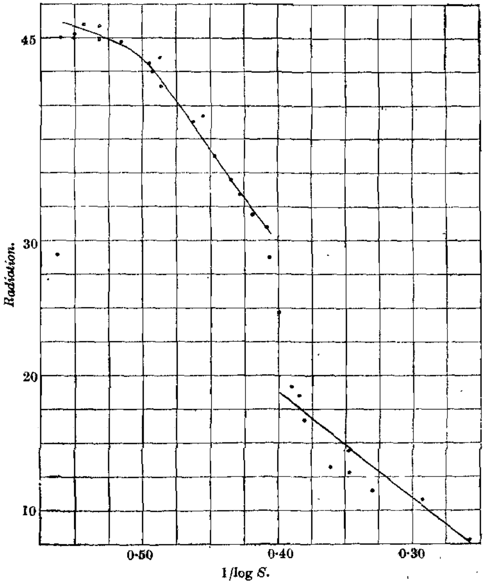


TABLE II.

Expt. No.	H_2, %.	Maximum deflexion (cm.).		Area (in arbitrary units).		Expt. No.	H_2, %.	Maximum deflexion (cm.).		Area (in arbitrary units).	
585		6·70		29·7		579		5·30		19·2	
586		7·00	6·9	30·7	30·0	580	0·016	5·35	5·3	20·0	19·3
587		6·90		29·6		581		5·25		18·8	
592		6·65		28·1		582		5·20		19·2	
593	0·0014	6·40	6·3	25·0	25·4	604		5·40		21·4	
594		6·20		24·6		606	0·016	5·20	5·3	19·0	19·7
595		6·05		23·9		607		5·25		19·6	
596		5·90		23·4							
597	0·0071	5·80	5·9	22·6	22·6						
598		5·85		21·7							
599		5·95		22·6							

room. The dry standard mixture was then introduced into the bomb and left for a period of time (one hour) sufficient for complete mixing with the water introduced previously. The time of saturation with water was increased until reproducible results were obtained. Erratic results, obtained when the bulb containing ice was kept below 0°, were probably due to the great absorptive

FIG. 7.



capacity of the walls of the bomb for water vapour. It was not found possible to complete the composition–radiation curve for water vapour. The results obtained from mixtures saturated at temperatures above 0° are here compared with those for hydrogen :

H_2O or H_2, %		0·00	0·60	1·02	1·95
Mean deflexion (cm.)	H_2O	57·7	13·6	10·4	6·8
	H_2	57·7	10·0	8·8	8·8

Johnson (*Phil. Mag.*, 1928, **5**, 301) showed that 2·3% of the gross heat of combustion was emitted as radiation for a mixture of $2CO + O_2$ containing 1·95% of water vapour. Taking this figure as a basis for calculation, we find that 19·5% of the heat of combustion is emitted in the case of the gas free from hydrogen.

Fortunately, it was possible to complete the radiation–log speed curve with water, since for this purpose it was not necessary to know the percentage of water vapour in the mixture. The results are shown in Fig. 7. The upper portion of the curve, corrected to values proportional to the radiation emitted, is given in Fig. 6, curve II. These results show that qualitatively the action of water and hydrogen is the same. The curve for water lies a little to the left of that for hydrogen.

Ionisation Phenomena.—The employment of the Einthoven galvanometer in the measurement of the speeds of flame has led to the accumulation of a certain amount of information on the effects of the addition of hydrogen on the ionisation in the flame. The information is qualitative in significance, for no attempt was made to obtain quantitative results. The figures in Table III are the means for a large number of experiments.

TABLE III.

H_2, %.	Velocity of flame (cm./sec.).	Maximum conductivity (arbitrary units).	Persistence of ionisation (sec.).
0·00	51·0	10	0·25—0·35
0·01	150	50	0·16
0·016	175	80	0·11
	237	90	0·10
0·023	409 *	150 *	0·06 *
	281	130	0·08
0·043	394 *	200 *	0·05 *
0·1	1150	360	0·03
0·5	1883	600	0·02
2·0	4740	1200	0·01

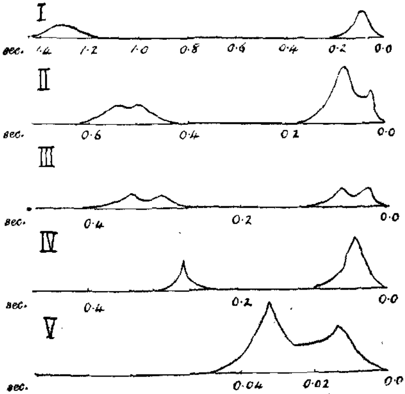
* Lower curve, Fig. 4.

The maximum conductivity increases 120-fold on passing from the dry mixtures to those containing 2% of hydrogen. The effect of the addition of larger quantities of hydrogen has been studied previously by Saunders and Sato (*Trans. Faraday Soc.*, 1927, **23**, 254).

The character of the Einthoven records undergoes marked changes as the percentage of hydrogen in the flame increases. With no hydrogen, the deflexions are single and very broad. On the addition of 0·01% of hydrogen or less, double peaks make their appearance at each deflexion, and this character is retained by the explosions represented on the upper curves in Figs. 3 and 4. Below the step on the radiation curves, the ionisation peaks become single

and give much sharper maxima. The experiments giving radiation values on the lower curve show single maxima of this type without exception. The typical double maxima of the upper curve suddenly give way to the sharp peaks of the lower region. Typical curves are shown in Fig. 8. In the earlier experiments (J., 1928, 280), the Einthoven records were either of type II or III. The "dried" gas was not sufficiently freed from water to give the maximum radiation from the flame, the minimum speeds of flame, or curves of type I.

Fig. 8.



I. 0·00% H_2; R = 45·1 *cm.*; V = 52·9 *cm./sec.*
II. 0·01% H_2; R = 43·2 *cm.*; V = 148 *cm./sec.*
III. 0·023% H_2; R = 37·6 *cm.*; V = 227 *cm./sec.*
IV. 0·023% H_2; R = 23·6 *cm.*; V = 243 *cm./sec.*
V. 0·5% H_2; R = 10·2 *cm.*; V = 2200 *cm./sec.*

In the present series, the pump used to remove traces of water from the walls of the bomb was more efficient than that employed in previous work.

Combustion of the Gases.—Analysis of the gases left in the bomb after combustion showed that about 10% of the carbon monoxide was unburnt. This percentage did not change very much throughout the above series of experiments, indicating that a definite fraction of the gas was chilled by the walls of the bomb in all cases:

H_2, %	0·00	0·10	2·0
Combustion, %	88·1	90·2	91·9

Radiation from the Hot Gases in the Flame.—The investigations of Paschen (*Ann. Physik*, 1894, **52**, 214) show that carbon dioxide emits its typical radiation at high temperatures, so that some part of the radiation from the flame must be due to thermal causes. The thermal emission will be the greater the slower the cooling of the products of combustion, and for a large mass of burning gas which cools slowly, the thermal emission would be expected to mask any chemiluminescence that may possibly occur. It is clear, therefore, that the chemical effects are best studied under conditions of rapid cooling. The incompleteness of combustion shown by the above figures indicates that in our experiments the cooling is rapid. The phenomena described in this paper could not be observed at all accurately in the larger bombs used by David (*Phil. Mag.*, 1920, **38**, 66). In large explosion vessels, the infra-red emission from the flame will consist mainly of radiation from the hot gases, and the effect of water or hydrogen on the radiation emitted will be very much smaller than in the above experiments.

This appears to be the case from experiments of Bone, Townend, and Scott (*Proc. Roy. Soc.*, 1928, *A*, **120**, 553), where at 64·4 atmospheres initial pressure, the addition of water did not increase the pressure generated in the explosion vessel. This would be expected were the radiation losses the same in the presence of water as in its absence. At high pressures, the increased rate of molecular collision, the increased absorption of radiation by carbon monoxide, and a relatively slow rate of cooling would militate against the observation of the above effect.

The best conditions for the study of chemiluminescence from flames are provided by low-pressure flames under conditions of rapid chilling. The results obtained will throw light on the mechanisms occurring in flame, and the information gained will be of value not only for the interpretation of low-pressure flames, but also for those flames where the conditions are such that the chemiluminescence is masked by the thermal emission.

Discussion of Results.

Chemiluminescence.—The large decrease in the emission of radiation from the flame, which accompanies the addition of small quantities of hydrogen (a reduction of 30% for 0·016% of hydrogen) is a confirmation of the view expressed by von Helmholtz that the radiation from flames is very largely chemiluminescence. The reduction in the emission cannot have been brought about by changes in the extinction coefficient of the gases due to the addition of hydrogen. The percentage of this gas producing the effect is so small that neither it nor the water produced from it can absorb

infra-red radiation to a sufficiently great extent to account for such a marked reduction. Another explanation of the result, *viz.*, that *the temperature of the flame is reduced* by *the addition* of *hydrogen*, is also unsatisfactory. The fact that the flames containing hydrogen lose less radiation than those of the hydrogen-free gases must mean that the former give the *hotter flame*.

If further confirmation of the view of von Helmholtz be needed, it is to be found in the behaviour of the flame on dilution by inert gases. The emission of radiation during the combustion of carbon monoxide is the greater the lower the temperature of the flame (compare *Ind. Eng. Chem.*, 1928, **20**, 1009).

The emitters of the radiation are the freshly formed molecules of carbon dioxide, which are activated as the result of the chemical change (3) (see p. 1124). These molecules may become deactivated by the emission of this energy as radiation (4), or by collisions of the second kind (5). It is possible to account for the decrease in the radiation on addition of hydrogen by ascribing to this gas, or to one of its products in the flame, a property which is possessed to a smaller extent by other gases, *viz.*, that it can readily remove the internal energy of carbon dioxide molecules by collision. This process is indicated by equation (5), the occurrence of which decreases the number of molecules deactivated by (4). Thus the emission of radiant energy is reduced.

An alternative explanation is that the hydrogen brings about a reduction in the radiation by modifying the mechanism of the reaction, thus :

$$(7)\ CO + H_2 + O_2 \longrightarrow CO_2' + H_2O.$$

It is conceivable that molecules of carbon dioxide so produced may not be activated to the same extent as when produced by (3). The chemiluminescence from molecules of carbon dioxide when produced by reaction (7) may be quite small. This also applies to the Dixon mechanism [(1) and (2), p. 1124].

General Characteristics of Flames containing Hydrogen.—The Einthoven records indicate that there are at least three distinct processes involved in the combustion of carbon monoxide in the presence of hydrogen. The flame of the hydrogen-free gases differs from one containing up to 0·04% of hydrogen, which in turn differs from one containing above this percentage. The dry flame passes into the second type of flame without discontinuity occurring in the speed of flame movement or in the radiation emitted. These properties change gradually, the former increasing and the latter decreasing as hydrogen is added. The flame containing less than 0·04% of hydrogen differs from that of the gases containing no

hydrogen in that in the former the flame is composite in character, possessing two distinct zones of ionisation.

The second type passes into the third more abruptly. There is a rapid fall in radiation at nearly constant speed of flame, and the two zones of ionisation are replaced by one. The third type is the only flame which occurs with the production of sound.

Interpretation.—At the present time, insufficient is known about the phenomena of flame to make it possible to interpret these results with any degree of completeness. The value of any interpretation suggested to account for the facts will lie mainly in its usefulness as a working hypothesis and in its suggestiveness for further experiments.

It is suggested that the nature of the flame reactions when less than 0·02% of hydrogen is present is different from that at higher percentages. If we designate the reaction occurring at low concentrations of hydrogen by A. and that at high concentrations by B, then the interpretation of the step on the above curves is that reaction A is more rapid at low, and reaction B more rapid at high, hydrogen concentration. At the step itself, it is suggested that reactions A and B possess similar speeds, and, in this region, slight changes in the conditions of firing, etc., lead to the predominance of either reaction in any particular experiment.

In the region where A is dominant, there are two ionisation maxima on the Einthoven records. These maxima are an indication that the flame is divisible into two parts following one another, and that possibly reaction A occurs in two distinct stages. Since the double maxima disappear below the step, these two stages may occur simultaneously in reaction B.

Logarithmic Relationship between Speed of Flame and Radiation.—The logarithmic relationship found to hold between speed and radiation (see Figs. 4 and 6), which resembles that between the velocity coefficient of chemical change and temperature, can be expressed as $1/\log S' = -Nr' + M$, where S' is the speed when the radiation $= r'$, or $\log S' = 1/(M - Nr')$, M and N being constants. When $r' = 0$, $\log S_m = 1/M$, S_m being the maximum speed; and hence

$$\log S_m - \log S' = Nr'/M(Nr' - M) \quad . \quad . \quad . \quad (8)$$

This equation can be derived from the Arrhenius equation $\log k = C + A/RT$. Stevens (*Ind. Eng. Chem.*, 1928, **20**, 101 has shown that the speed of flame of mixtures of carbon monoxide and oxygen at constant pressure is given by $S = K[CO]^2[O_2]$, which is of the same form as the velocity equation $dx/dt = k[CO]^2[O$ indicating that there is a linear relationship between K and so

velocity coefficient, k, which controls the speed of flame. The precise significance of k in the flame is not known. It may be that the velocity coefficients of the reaction change according to the same law across the flame front for all mixtures of carbon monoxide and oxygen, and the value of k for any zone in the wave front may be said to control the speed of flame.

In our experiments with this flame, the concentrations of carbon monoxide and oxygen are constant throughout. The percentages of hydrogen and the losses of radiation, however, vary. In each zone in a flame, the loss of radiation is proportional to the amount of chemical change. The temperature of these zones will also be proportional to the amount of chemical change, so that any variation in the total radiation from the flame will probably affect the temperature of each zone by a constant fraction. This will be only approximately the case, since the specific heats vary with temperature, and the emission of radiation varies slightly with the temperature. This fraction will equal cr'/T, where c is a constant, r' is the loss of radiation, and T the temperature at any point in the flame front when there is no loss of radiation.

Now, since $S' = k[CO]^2[O_2]$, where k is the velocity coefficient at any point in the flame front, $\log S' = C' + A/RT'$, where $T' = (T - cr')$ and C' is a constant. Hence

$$\log S' = C' + A/R(T - cr'),$$
$$\log S_m = C' + A/RT,$$
$$\text{and } \log S_m - \log S' = Acr'/RT(cr' - T) \qquad (9)$$

This is of the same form as (8), but until the result obtained by Stevens is more clearly understood, the similarity cannot be stressed. Also, the speeds given in this paper are average speeds of flame movement, and if any arrest in the speed of flame occurs between the electrodes used in measuring this speed, the applicability of the above argument is weakened.

Summary.

The effect of hydrogen and water on the emission of radiation and the speed of flame of mixtures of hydrogen and oxygen has been studied. On addition of hydrogen or water the radiation from the flame decreases as the speed of flame increases. There is little difference between the effects of the two gases. At 0·02—0·04% of hydrogen, there is a critical region, where the radiation from the flame falls abruptly and the properties of the flame undergo a marked change. The radiation–composition and radiation–speed curves give a step at this point.

Logarithmic relationships are found to hold between the speed of

flame and the radiation emitted. These apply to mixtures above and below the step respectively. They afford support for the "energothermic" theory of the catalysis.

The step on the radiation curves is considered to be due to a change in the nature of the chemical reaction.

Our thanks are due to Imperial Chemical Industries, Ltd., for a grant for the purchase of apparatus, and one of us (F. R.) wishes to express his indebtedness to the Department of Scieutific and Industrial Research for a maintenance grant.

THE UNIVERSITY, BRISTOL. [*Received, November 27th*, 1928.]

CL.—*The Effect of Gases on the Electric Charges Developed by Heated Metals.*

By DONALD HUGH BANGHAM and DOUGLAS ROSTRON LEWIS.

IT was shown by Hartley (*Proc. Roy. Soc.*, 1914, *A*, **90**, 61) that a metal surface, when heated in contact with different gases, tends to become charged to a definite potential characteristic of each gas. Working with a roll of gold gauze, suspended inside a glass vessel by a sealed-in gold wire which connected it to an electrometer, he found that when the apparatus was heated, not only did the gauze become charged, but the effect could be repeated an indefinite number of times between successive earthings. It follows that if the gauze were maintained—by earthing or otherwise—at a potential other than the equilibrium one, the system must have furnished a continuous current tending to produce the equilibrium conditions. It was to elucidate the nature of these currents and the chemical changes associated with their production that the present investigation was undertaken. Hartley's own suggestion is that the effects are due to "deeply occluded" gas leaving the metal in a charged condition.

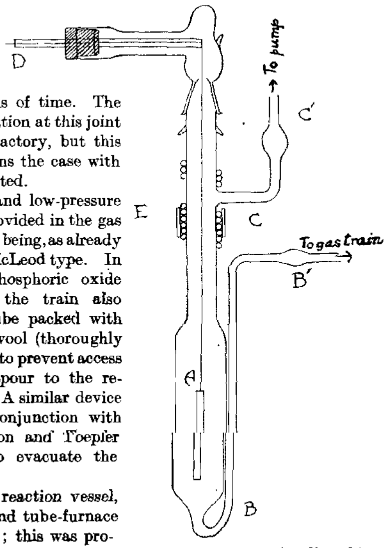
Whilst endeavouring to reproduce Hartley's experimental conditions, the authors have centred their attention, not on the equilibrium potentials themselves—it soon became evident that only qualitative agreement with Hartley's results could be hoped for—but on the rate of development of the charges, *i.e.*, the magnitude of the currents.

EXPERIMENTAL.

Apparatus.—A sketch of the reaction vessel is shown in Fig. The wide Jena-glass tube, A, was drawn down at both ends to make a cylindrical bulb about 10 cm. long. The quill tubes,

and C, sealed to soda-glass leads at B′ and C′, communicated respectively with the gas train and the pump. The gold gauze, rolled into a narrow cylinder 5 cm. long, was suspended centrally in the vessel by a gold wire carried through a glass capillary, D, secured in its place by an ebonite plug. The seals between wire, capillary tube, plug, and side arm of the reaction vessel were successfully made with sealing wax, a McLeod gauge sealed to the gas train showing no trace of leak when the apparatus was evacuated and left standing for long periods of time. The electrical insulation at this joint was also satisfactory, but this was by no means the case with other forms tested.

FIG. 1.



Both high- and low-pressure gauges were provided in the gas train, the latter being, as already stated, of the McLeod type. In addition to phosphoric oxide drying tubes, the train also contained a tube packed with silvered glass wool (thoroughly freed from gas) to prevent access of mercury vapour to the reaction vessel. A similar device was used in conjunction with the condensation and Toepler pumps used to evacuate the apparatus.

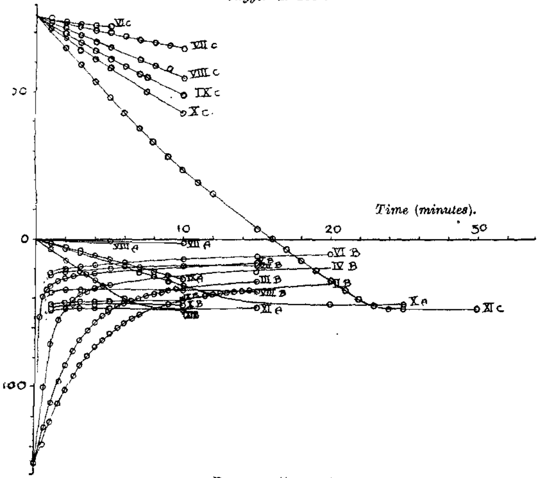
To heat the reaction vessel, a specially wound tube-furnace was constructed; this was provided with an earth-connected lining to screen out the disturbing effects of the heating current. With proper precautions, it was found that the heating current could be switched off for some seconds without in any way influencing the results obtained.

The electrometer, which was of the Dolezalek pattern, was shielded by enclosing it in a tin box supported on shock-absorbers. One pair of quadrants was permanently connected to earth, and the second to earthing and "mutating" keys placed inside the box.

The mutating key permitted connexion to be made, as desired, to the gold electrode, the potentiometer, or both. Careful experiments were made to test the trustworthiness and sensibility of the electrometer system, to determine its optimum working conditions, and to eliminate stray fields by the provision of suitably placed screens and guard rings. Throughout the series of experiments with gases, the electrometer needle was charged to 132 volts; the

FIG. 2.

Oxygen at 468°.



Pressures (in mm.).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
152	59	25	8·0	1·83	0·307	0·038	0·0175	0·0081	0·0023	<0·000

phosphor-bronze suspension used gave, under these conditions, a deflexion of 52 scale divisions per volt.

Experiments with Oxygen.—Dry oxygen was admitted to the reaction vessel to a pressure of *ca.* 400 mm., and the temperature gradually raised. No appreciable charging-up was observed at Hartley's working temperature (*ca.* 370°), and it was not until about 100° higher that the charging rate became conveniently large

Systematic measurements were made at two temperatures, *viz.*, 468° and 497°, the procedure being as follows: (i) The insulated quadrants were placed in communication with the gold electrode, the earthing key being down; the latter was then lifted and the deflexion of the needle noted after definite intervals of time (see curves A, Fig. 2). (ii) The gauze was charged to − 3 volts and the deflexion noted; connexion to the potentiometer was then broken, and the rate of discharge observed (see curves B). (iii) The gauze was charged to + 3 volts and the same procedure followed (curves C).

Part of the gas was then removed by means of the pump, and a new series of measurements taken at a lower pressure. The process was continued until the pressure of gas remaining could no longer be measured with accuracy.

It was found important to adopt a uniform plan of procedure throughout the experiments, since the results obtained depended (as indicated below) on the past history of the gold gauze. For this reason experiments (i), (ii), and (iii) were carried out at each pressure in the order stated.

Discussion of Results with Oxygen.—The results of experiments carried out with oxygen at 468° are shown graphically in Fig. 2. A study of these diagrams leads to the following conclusions:

(i) The rate of attainment of the final equilibrium potential is considerably retarded by the presence of oxygen, even at low pressures.

(ii) The non-appearance of the effect observed by Hartley (*i.e.*, the charging-up from zero potential) at high oxygen pressures is probably due to this retardation, and does not indicate that the equilibrium potential is zero in such cases.

(iii) Increased pressure of oxygen causes a marked shift of the equilibrium potential towards the positive side, as indicated by the intersection of the high- with the low-pressure curves B in Fig. 2. It remains an open question whether, at still higher pressures, this displacement would be sufficient to give rise to the positive equilibrium potential observed by Hartley in the case of oxygen.

(iv) The mode of approach to the equilibrium potential is widely different according as the equilibrium value is approached from the positive or from the negative side. In the latter case, the rate of change is a highly sensitive function of the momentary potential; in the former, it is markedly insensitive, the rate being nearly uniform.

Explanation of Curves in Terms of Thermionic Emission Theory.—The dissimilarity in form between the B and C curves is readily

explicable if it be supposed that the leakage currents are carried mainly or entirely by ions of one sign between the hot metal and the glass wall of the containing vessel, which acts as a second electrode. Since, at the low temperatures used, it is the positive emission which is predominant, it may be safely presumed that the carriers are positive ions.

Supposing a positive potential to be given to the gauze (curves C), a very weak field suffices to drive all the ions emitted by it across to the glass wall, simply on account of the size of target which the latter offers. For the same reason, ions emitted by the wall are also made to return. The current is therefore saturated, or nearly so,* and does not decay until the potential of the metal has fallen nearly to its final or equilibrium value.

If, on the other hand, a negative potential of 3 volts is given to the metal, the carriers are the positive ions emitted by the glass wall. There is little difficulty in crediting glass with the power of emitting such ions: it was shown by Richardson that the positive emission from a well glowed-out wire could be enormously increased if the walls of the glass containing vessel were only slightly heated.† Since, however, the metal electrode offers only a small target as compared with the emitting surface, the proportion of ions reaching the former *is a highly sensitive function of the field strength. The feebler the field, the greater will be the proportion of ions reabsorbed* by the wall.

The Nature of the Ions.—As regards the identity of the positive carriers, there are two possibilities to be considered: they may be either (i) charged atoms or molecules of oxygen, or (ii) ions of the type shown by Richardson to result from heating new metal wires in a vacuum. Type (i) was found by Richardson (*op. cit.*, pp. 30 *et seq.*) to result when platinum is heated in oxygen to temperatures of 700° and above.

In striking contrast to the results of the experiments here described, Richardson found that this emission *increased* with the pressure of oxygen, the saturation currents being nearly proportional to the pressure when the latter was small. There is little reason, therefore, to identify as type (i) the emission from a gold surface at a temperature some hundreds of degrees lower.

On the other hand, if the above explanation of the function of

* As will be shown later, the ionic currents were far too small to give rise to "space charge" effects.

† Richardson, "The Emission of Electricity from Hot Bodies," Longmans, 2nd edtn., p. 203. Since the usual procedure in thermionic experiments is to work with electrically-heated wire sealed by heavy leads inside a cold vessel, it is clear that the emissive power ascribed to glass would not be a disturbing factor.

the glass wall is correct, we must ascribe to the metal gauze all the properties of "new" wires described by Richardson, and identify the ions as those of potassium and sodium (*idem, ibid.*, p. 210), for even at the high temperatures used by him, Richardson found that unless the metal filament were well glowed-out, these ions, though present only as impurities, entirely masked the positive emission due directly to the oxygen. So far from this being practicable in our experiments, the conditions were actually those which favoured the revival of type (ii) emission in "glowed-out" wires: there can be little doubt, therefore, that the observed effects were due to alkali-metal carriers.

The Rôle of the Gas.—Since, after the partial removal of gas from the system, the leakage currents did not attain the values characteristic of the new pressure until after the lapse of some time, it follows that the electrical effects were conditioned, largely at any rate, by absorbed or occluded oxygen, and not directly by the pressure of dead-space gas. On this basis only does it become explicable that, although the general effect of a pressure reduction was invariably to increase the leakage currents, the gradual accumulation of occluded gas in the dead space (following such a reduction) was associated with an increase in the current strengths under corresponding conditions.

The following table, based on a series of experiments carried out at 497°, illustrates this point; it is important to note that since the currents approximate to saturation, the results are not affected in any way by what is happening at the glass wall.

The values of the "limiting deflexion" given in the table indicate that a similar argument applies also to the "equilibrium" potential, which displays a noticeable drift with time. In this case, however, the drift may be partly associated with processes taking place at the second electrode, *i.e.*, the glass wall.

Expt.	Time after pressure reduction (mins.).	Deflexion in first minute after earthing (mm.).	Limiting deflexion (mm.).	Pressure (mm.).
XII A′	16	—20	—	—
	25	—	—40·5	0·0102
XII A″	28·5	—23	—	—
	38·5	—	—41·5	0·0105
XII A‴	68	—35	—	—
	70	—	—42·9	0·0116

It has been established by Richardson and Robertson (*Phil. Mag.*, 1922, **43**, 162) that the influence of occluded gas on the electronic emission of metals is due primarily to their effect on the contact *E.M.F.*, which is a measure of the work ϕ necessary to remove the electron from the interior of the metal to a point at

infinity. The effect of gases generally, and of oxygen invariably, being to depress the electronic emission, it follows that ϕ is increased thereby. Since an exactly corresponding effect must also be operative in the case of the positive emission, it seems at first sight that the effect of oxygen should be to increase this emission from the metal. There is, however, a material as well as the electrical factor here to be considered (Richardson, *op. cit.*, p. 243), and it does not therefore follow that an influence which depresses the negative emission must stimulate the positive: on the contrary, the work done in removing both a positive ion and an electron to infinity must depend on the magnitude of the cohesive force in the interior of the metal, which may be considerably influenced by the presence of occluded gas (Bangham, *Phil. Mag.*, 1928, **5**, 737).

Measurement of True Ionic Currents.—If a probable value is assigned to the capacity of the electrical system of which the insulated quadrants and the gold electrode form the extreme elements, approximate values of the currents may be calculated by taking tangents to the potential–time curves illustrated in Fig. 2. On the basis of a capacity of 10^{-10} farad, the family of curves VI to XI C is found to represent initial currents ranging from 5×10^{-14} to 3×10^{-13} amp. These figures do not necessarily, however, represent the true ionic currents, for the reason that glass, even when hot, is but a poor conductor, and, by allowing the charges partly to accumulate on its surface, may give rise to induction effects. This accumulation continues until the leakage current through the glass (passing perhaps to the outer surface of the vessel, and thence to the earth-connected coil of piping) becomes equal to the ionic current passing between the electrodes.

To eliminate these secondary effects from the measurement of the currents and from the determination of the characteristic potential–current curves, a static method of measurement was adopted. The apparatus was so modified that the gold electrode could be connected to the potentiometer either (i) as before, by a lead of negligible resistance, or (ii) through a known liquid resistance (about 10^{12} ohms).

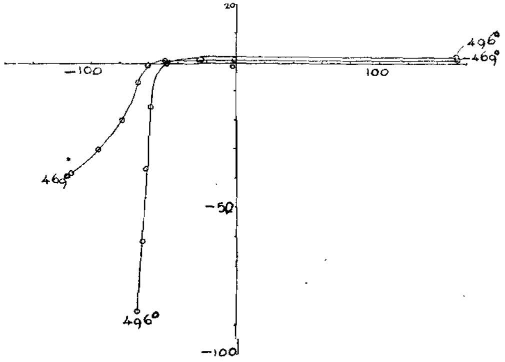
The procedure was then as follows: A known potential was given to the gauze, and the deflexion noted. By means of the mutating key the high-resistance lead was then substituted for the direct one. Under these conditions the ionic current manifested itself by setting up an appreciable *P.D.* between the potentiometer terminal and the gold electrode. To measure the current, now flowing equally through all parts of the system, it was necessary only to note the difference between the new and the old deflexion, and

divide the corresponding voltage by the resistance of the liquid column.

The graphs in Fig. 3 are typical of the results so obtained. The flat portions on the right represent the saturation positive-ion currents passing from the gauze to the wall when the former is positively charged; these currents were of the order of 10^{-13}—10^{-14} amp. according to the temperature of the system and the pressure of the gas. With the gauze negatively charged, much greater currents (up to about 10^{-12}) were found, and here, as the graphs indicate, there was no approach to saturation.

FIG. 3.

Current–potential curves for oxygen vacuum.



Abscissæ = Potential of gold.
Ordinates = Resultant current from gold.

A comparison of the saturation currents at the two experimental temperatures (and otherwise corresponding conditions) permits a rough calculation to be made of the characteristic constant b in the thermionic equation $i = A\sqrt{T}e^{-b/T}$, where i is the (saturation) current and A a constant. Such calculations, though subject to considerable uncertainty on account of the smallness of the temperature range, indicate that b probably does not exceed $1{\cdot}5 \times 10^4$. Since this constant never appears to fall below 3×10^4 in the case of the electronic emission from different metals, whilst in the case of the positive emission it certainly takes much smaller values ($1{\cdot}34 \times 10^4$ in the case of silver; Richardson, *op. cit.*, pp. 205, 206;

Brit. Assoc. Reports, 1904, 473), there can be little doubt as to the sign of the charges carrying the current.

Experiments with Nitrogen and with Hydrogen.—Following the series described, similar experiments were carried out with nitrogen and hydrogen at 468°. The former gas gave results strikingly similar to those with oxygen. The equilibrium potentials were invariably lower (*i.e.*, more negative) and the saturation currents greater than at corresponding pressures of oxygen.

With hydrogen the results were somewhat different. Even at the lowest working pressure (0·0238 mm.) the equilibrium potential was about 0·30 volt lower than the standard *in vacuo* measurement of 0·90 volt, whilst a 100-fold increase of pressure was without appreciable influence on its value.

With regard to the magnitude of the currents, hydrogen at 80 mm. had very little effect on the initial current from the gold to the glass when the former was charged to + 3 volts and then insulated, although it had some effect on the initial "post-earthing" current. At lower pressures the effect of this gas was markedly to stimulate the positive-ion emission from the metal. At a pressure of 0·0238 mm. the saturation current was nearly four times its normal *in vacuo* value.

Summary and Conclusions.

(1) The attempt here described to reproduce quantitatively the phenomena observed by Hartley has proved unsuccessful. This is by no means surprising in view of the known dependence of the effects in question on the past history of the metal.

(2) Nevertheless, at the temperature used, oxygen was found to give rise to a positive displacement of the "equilibrium potential," and hydrogen to a negative. Whilst the displacement caused by the former gas was found to be a function of its pressure, that of the latter was independent of the pressure over a wide range.

(3) The charging-up of the metal is in the nature of a Volta effect, depending on an intrinsic difference of potential between the metal and the glass wall of the containing vessel. As such, it is dependent for its manifestation (but not for its existence) on the dynamical exchange of ions between the two surfaces.

(4) Under the conditions of the experiments, the ions in question were neither electrons nor charged oxygen corpuscles, but were probably of the same nature as those found by Richardson to be emitted from "new" wires of various metals; they are therefore identified as ions of potassium and sodium.

(5) The power of the metal to emit these ions is diminished by the presence of occluded oxygen or nitrogen. Hydrogen at low

pressures stimulates the emission—a fact undoubtedly connected with the direction of its influence on the equilibrium potential.

We wish to acknowledge the receipt of grants from the Royal Society and from the Brunner Mond Research Fund which partly defrayed the cost of this and parallel investigations.

EGYPTIAN UNIVERSITY, CAIRO. [*Received, March 20th, 1929.*]

CLI.—*The Oxidation of Tungsten: Evidence for the Complexity of Tungstic Oxide,* WO_3.

By JOHN STANLEY DUNN.

THE rate of oxidation of a metal such as tungsten is governed by *the rate of diffusion of oxygen through the protective layer* of tungstic oxide formed upon the metal as a result of the reaction. In these circumstances the oxidation law is parabolic, *i.e.*, $W^2 = Kt$, where W is the weight of oxygen absorbed in time t, and K is a constant (Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529). For most metals K increases regularly with temperature according to the equation $K = Ae^{-Q/R\theta}$, where A and Q are constants, θ is the absolute temperature, and e and R have their usual significance (Dunn, *Proc. Roy. Soc.*, 1926, *A*, **111**, 207).

Since the properties of tungstic oxide determine the rate of oxidation of tungsten, abnormal variations in the latter are symptomatic of abnormal changes in the former. During the course of an investigation of the action of air upon tungsten at temperatures between 700° and 1000°, the rate of oxidation was found to vary abnormally between 850° and 900°. This is shown by the following values of K (in g.^{2}/cm.^{2} per hour) and by Fig. 1, in which log K is plotted against $1/\theta$.

Temp. (C.)	700°	800°	850°	875°	900°	925°	950°	1000°
$K \times 10^5$	1·61	16·6, 22·5	40	18·0	17·9, 13·4	62·5	116	461

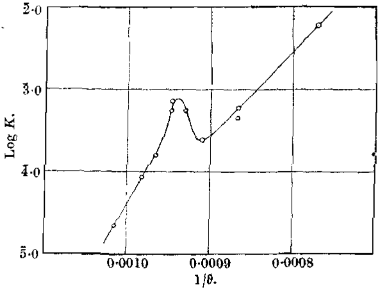
It was suspected at first that the oxide was undergoing a sintering action at temperatures above 850°, giving in consequence a less permeable oxide film. Such phenomena have been encountered in the cases of aluminium, copper, and zinc (Pilling and Bedworth, *loc. cit.*; Dunn, *loc. cit.*, pp. 207, 215), but in these cases the form of the oxidation curve during sintering undergoes modification and is no longer a quadratic parabola with respect to time, whereas, for tungsten at 875°, the parabolic law was obeyed perfectly, as

may be seen from the constancy of K (in g.^{2}/cm.^{2} per hour) for the oxidation at this temperature :

t (mins.)	10	20	30	50	60	80	90	105	120	170
$K \times 10^4$	1·87	1·69	2·02	1·95	1·94	2·02	1·94	1·93	1·93	2·18

It is therefore certain that the tungstic oxide is in equilibrium from the commencement of the experiment. The only hypothesis in accordance with the facts is that tungstic oxide is not a pure *unary substance but consists of a mixture* of α-WO_3 *and* β-WO_3, the equilibrium between the two modifications shifting with temperature. The β-modification, which is formed in excess at higher

Fig. 1.



temperatures, is less permeable to oxygen than the α-form, and in the temperature range in which the change from excess of β to excess of α occurs, a kink is found in the oxidation–temperature curve.

Some support for this hypothesis is afforded by the colour of the oxide : at the ordinary temperature it is lemon-yellow, but at higher temperatures it changes to quite a deep orange.

The author is indebted to the Council of the British Non-ferrous Metals Research Association for permission to publish this paper.

[*Received, April 3rd,* 1929.]

CLII.—*The Partial Esterification of Polyhydric Alcohols. Part VIII. The Proposed Standards of Reference in Work on the Configuration of Glycerol Derivatives.*

By ARTHUR FAIRBOURNE.

SINCE the publication of Part V (J., 1926, 3148; *Ann. Reports*, 1927, 90), showing the illusory nature of synthetic processes for the preparation of "β"-mono-derivatives of glycerol, Helferich and Sieber (*Z. physiol. Chem.*, 1927, **170**, 31; 1928, **175**, 311) have made the true β-monobenzoate by a method which seems capable of general application for β-esters, and Hill, Whelen, and Hibbert (*J. Amer. Chem. Soc.*, 1928, **50**, 2235) have synthesised the true β-methyl ether, believed to be the first true β-ether of glycerol ever isolated.

Hibbert, Whelen, and Carter (*J. Amer. Chem. Soc.*, 1929, **51**, 302), referring to Part V of this investigation, and emphasising the difficulties of identification which have resulted, propose that the ethers of glycerol should now be adopted as the standards of reference in work on configuration, and mention that the isolation of the new compound renders available all five of the possible glycerol methyl ethers :

I. α-Monomethyl ether (Irvine, Macdonald, and Soutar, J., 1915, **107**, 337).

II. β-Monomethyl ether (now isolated).

III. αβ-Dimethyl ether (Gilchrist and Purves, J., 1925, **127**, 2735).

IV. αγ-Dimethyl ether (Zunino, *Atti R. Accad. Lincei*, 1897, **6**, 348).

V. αβγ-Trimethyl ether (Gilchrist and Purves, *loc. cit.*).

Before these ethers are used as standards of reference, however, it is desirable that their structures should be thoroughly established : I, II, and V are clearly trustworthy, but it is doubtful (see Part VII, this vol., p. 129) whether the "αβ"-dimethyl ether (III) really has the structure which Gilchrist and Purves assign to it. For the same reasons, the structure of the "αγ"-dimethyl ether (IV) also ought to be regarded as unproven.

These two supposed isomerides have been examined and found to be identical. One dimethyl ether (III or IV), therefore, is still unknown.

A communication will be made later on the similar preparation

recorded by Gilchrist and Purves (*loc. cit.*) for the "α"-methyl ether (I).

EXPERIMENTAL.

Glycerol Dimethyl Ether (III or IV).—Glycerol "$\alpha\beta$"-dimethyl ether, prepared from $\alpha\gamma$-dichlorohydrin by Gilchrist and Purves' method (*loc. cit.*), and glycerol "$\alpha\gamma$"-dimethyl ether, prepared from epichlorohydrin by Zunino's method (*loc. cit.*), could not be distinguished from each other, both possessing specifically identifying properties recorded by Gilchrist and Purves. As glycerol isomerides of low molecular weight, differing by the interchange of groups in the α- and β-positions, exhibit appreciably different characteristics, there is no doubt that the above products are identical. Their being so is in accordance with Zunino's own expectations. He pointed out that the two methods normally lead to an identical product, and instanced glycerol diethyl and di*iso*amyl ethers (Reboul, *Annalen*, *Suppl.*, 1862, **1**, 238), which were prepared in both these ways.

That Gilchrist and Purves' alternative preparation from $\alpha\beta$-dibromohydrin also yields the same product has already been proved by them (*loc. cit.*). The preparation has, however, been repeated, and the product found indistinguishable from either of the two specimens mentioned above.

This work has been closely paralleled by Boyd and Marle (J., 1901, **79**, 1221; 1908, **93**, 838; 1909, **95**, 1807), who, using phenol instead of methyl alcohol, investigated all three of these reactions and obtained an apparently identical glycerol diphenyl ether in each case.

p-*Nitrobenzoyloxydimethoxypropane*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_3H_5(OMe)_2$.—The glycerol dimethyl ethers obtained by the methods mentioned above (*viz.*, from $\alpha\gamma$-dichlorohydrin, from epichlorohydrin, and from $\alpha\beta$-dibromohydrin) were separately warmed (5 g.) with 4 g. of pyridine and 28 c.c. of a solution of *p*-nitrobenzoyl chloride in chloroform (containing 27·5 g. in 100 c.c.). After 48 hours, ether and water were added and the ethereal extract was washed with water, dilute sulphuric acid, dilute sodium bicarbonate solution and again with water, dried with calcium chloride, concentrated, and heated in the steam-oven for 1 hour. The product was induced to crystallise by scratching; after recrystallisation from light petroleum, it melted in each case at 43°, alone or when mixed with either of the other two (Found: $NO_2{\cdot}C_6H_4{\cdot}CO$, 56·0. $C_{12}H_{15}O_6N$ requires $NO_2{\cdot}C_6H_4{\cdot}CO$, 55·8%).

In view of the evidence of Hibbert, Whelen, and Carter (*loc. cit.*) that methoxy-groups do not migrate during esterifications of this

type, these mixed melting points serve to confirm the identity of (III) and (IV).

The author is indebted to the Chemical Society for a grant which has partly met the expense incurred in this work.

KING'S COLLEGE, LONDON. [*Received, March 13th, 1929.*]

CLIII.—*The Influence of the Intensity of Illumination on the Velocity of the Photochemical Union of Bromine and Hydrogen.*

By MAX BODENSTEIN, WILHELM JOST, and GERHARD JUNG.

BRIERS and CHAPMAN (J., 1928, 1802) recently investigated the influence of light intensity on the photochemical combination of bromine and hydrogen, and concluded that the reaction velocity is proportional to a power of the light intensity which varies between ½ and 1 and is always greater the weaker the light. From their experiments they found that the velocity of disappearance of "the catalyst, excited bromine molecules or bromine atoms," which causes the reaction is given by the sum of a uni- and a bi-molecular reaction

$$-dA/dt = C_1A^2 + C_2A \quad . \quad . \quad . \quad . \quad (1)$$

(A is the concentration of the catalyst) and that its mean life is about 0·063 sec.

The first observation is apparently in contradiction to the measurements of Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1925, **114**, 208), who found an exact proportionality between the reaction rate and the square root of the light intensity, and to their theory, that the catalyst, if we are to use this term, is actually bromine atoms. We have carried out a series of further experiments * which undoubtedly clear up these really only apparent discrepancies. According to these experiments, the velocity with which the catalyst disappears can, under certain conditions, be proportional to even the first power of the concentration, and, moreover, the mean life is of the same order of magnitude as in the work of Briers and Chapman.

Bodenstein and Lütkemeyer explained their results by assuming that the velocity of formation of bromine atoms is proportional to the light absorbed and that they are removed by recombination in

* They will appear shortly as the work of Jost and Jung in the *Zeitschrift für physikalische Chemie.*

the gas phase, the rate of this recombination being assumed to be proportional to the concentration of the atoms.

However, according to the theory (Jeans, "The Dynamical Theory of Gases," 2nd. edtn., 1916, p. 211; Herzfeld, *Z. Physik*, 1921, **8**, 132; Born and Franck, *ibid.*, 1925, **31**, 411) which has been developed in the meanwhile, the recombination of atoms is possible only in three-body collisions; a quasi-molecule, formed by the collision of two atoms, is not stable, but decomposes immediately if it cannot transfer its reaction energy by collision within its life period of *ca.* 10^{-13} sec. This means that the recombination of two atoms to form a diatomic molecule is a *termolecular* reaction. The velocity is dependent, not only on the concentration of the atoms, but also on the total pressure (the concentration of all the gases present). This leads to the following reaction mechanism for the formation of hydrogen bromide in light:

(1) $Br_2 + h\nu = 2Br$, velocity $= 2I_{abs.}$;
(2) $Br + H_2 = HBr + H$, vel. coeff. k_2;
(3) $H + Br_2 = HBr + Br$, vel. coeff. k_3;
(4) $H + HBr = H_2 + Br$, vel. coeff. k_4;
(6) $Br + Br = Br_2'$, vel. coeff. k_6;
(8) $Br_2' = Br + Br$, vel. coeff. k_8;
(9) $Br_2' + N = Br_2 + N'$, vel. coeff. k_9;

where Br_2' is the quasi-molecule and N any molecule at all. Instead of equations (6)—(9), Bodenstein and Lütkemeyer have simply (6) $Br + Br = Br_2$, which is not admissible according to our present ideas of molecule formation. The concentration of the molecules N which occurs in equation (9) is proportional to the total pressure at constant temperature—we may avoid considering the specific factors of individual gases in this case—and therefore we introduce this pressure in the following equations for the sake of convenience.

From the foregoing mechanism the following velocity equation is obtained (by a small approximation which is permissible if the pressure is not too high):

$$\frac{d\,[HBr]}{dt} = \frac{2k_2[H_2]\cdot\sqrt{I_{abs.}\cdot\frac{k_8}{k_6k_9p}}}{1+\frac{k_4[HBr]}{k_3[Br_2]}} \quad . \quad . \quad . \quad (2)$$

This equation differs from that obtained experimentally by Bodenstein and Lütkemeyer only by the factor $\sqrt{k_8/k_9p}$ which indicates a dependence upon the total pressure; and this dependence has been studied in our work.

At first a very large flask was used, from which samples of gas could be taken for analysis. In order to obtain intensive illumination the vessel was made in the shape of a ring (cross section

10×30 cm.; capacity 20 litres), and a lamp of 1-kw. capacity with a perpendicular spiral filament was placed within the ring. The apparatus was placed in an aluminium thermostat at 195°, and the reaction was measured over a pressure range of 4—400 mm. of mercury.

The factor $\sqrt{k_6/k_8 p}$ thus underwent a ten-fold increase between the highest and the lowest pressure, the velocity rising in the same manner. However, it was impossible to measure the intensity of the absorbed light in these experiments; furthermore, there arose considerations against the use of white light, because in the meantime the analysis of the absorption spectra of the halogens (Franck, *Trans. Faraday Soc.*, 1925, **21**, 3; Franck, Kuhn, and Roleffson, *Z. Physik*, 1922, **43**, 155) had shown that in the case of bromine a direct decomposition into atoms occurs at $\lambda > 5107$ Å.; and at lower wave-lengths, on the other hand, excited bromine molecules are formed, which decompose only on collision with other molecules, when this collision follows soon enough afterwards. Hence it became necessary to work with monochromatic light, of which the absorbed intensity could be measured. In this way in preliminary experiments it was shown that the wave-length has no influence: at the pressures employed, all excited bromine molecules decompose into atoms (Jost, *Z. physikal. Chem.*, 1928, **134**, 92).

For the main experiments the following method was used. The reaction vessel of quartz ($2 \times 4 \times 40$ cm.) was illuminated through its 4×40 cm. surface, and the concentration of bromine, and hence the progress of the reaction, was followed by measuring with a spectrophotometer a beam of light passing down its long axis. Heating, as before, was by means of an aluminium thermostat. In this arrangement the light intensity and the thickness of the reaction vessel were appreciably smaller than in the preliminary work—this is of importance for what follows.

The results now showed a large fall in reaction velocity with decreasing pressure, quite different from the results described above and from what was to be expected from equation (2).

The explanation of this phenomenon is that at low pressures and in a narrow vessel the bromine atoms, especially at low concentrations, *e.g.*, with weak illumination, are eliminated not so much by recombination in the gas phase, but rather by diffusion to the walls, where they are adsorbed and recombine. In the same way the completely analogous observation in our work on the photochemical formation of carbonyl chloride has been explained (Bodenstein, Lenher, and Wagner, *Z. physikal. Chem.*, in course of publication). It can be shown that the reaction velocity "constants,"

which are calculated from equation (2) and are of course no longer constant if the wall plays a part, are only a function of a magnitude

$$\pi = \text{const.}\ \sqrt{I_{\text{abs.}}}\ p/D \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(D is the diffusion constant of bromine atoms). The course of this function can be calculated, partly exactly and partly by approximation, and the observed values agree very well. It follows at once that in the case of the large reaction vessel the wall must be of no importance, because of the large light intensity and the dimensions of the vessel.

Accordingly, we can see that bromine atoms in *illuminated* bromine are used up in two processes :

(1) Recombination by three-body collisions in the gas phase the velocity of which is derived from equations (6), (8), and (9) :

$$-d[\text{Br}]/dt = [\text{Br}]^2 k_6 k_9 p/k_8{}^{*} \quad . \quad . \quad . \quad . \quad (4)$$

$= C_1[\text{Br}]^2$ at constant total pressure.

The constants can be calculated by combining the measurement of the light reaction with those of the dark reaction (see Bodenstein and Lütkemeyer, *loc. cit.*; Jung and Jost, *loc. cit.*).

(2) Recombination through diffusion to the walls, where they are absorbed until they combine, which process can be shown to be unimolecular at constant total pressure :

$$-d[\text{Br}]/dt = C_2[\text{Br}] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By superimposing both processes, one obtains the equation for the decrease in bromine atom concentration

$$-d[\text{Br}]/dt = C_1[\text{Br}]^2 + C_2[\text{Br}] \quad . \quad . \quad . \quad . \quad (6)$$

which is identical with the one found by Briers and Chapman. It can readily be seen that C_1 and C_2 are dependent on the pressure C_1 being directly proportional and C_2 inversely proportional to it. If Briers and Chapman had varied the ratio of their gases and the total pressure, they would certainly have found this influence of pressure.

Finally, we will calculate the actual value of the velocity coefficient and the mean life of the atoms from our measurements as found by Briers and Chapman. An uncertainty affects these calculations from the fact that these authors did not measure the light intensity and gave no data on the observed degree of combination. We may however, assume that this amounted to 10—30% of the bromine present and so, by comparison with Lütkemeyer's measurements we can obtain the missing values.

* Again we neglect a second-order term.

For $k_6 k_8 p / k_9 = C_1$ we get from our own measurements at thos pressures at which Briers and Chapman worked :

$$C_1 = 1{\cdot}55 \times 10^{11}.$$

In order to obtain good values for the mean life, τ_1, if the recombin ation occurs solely in the gas phase, we must know the concentratio of the atoms, and we obtain an approximate value as follows Lütkemeyer *found a combination of the bromine present of 10—30%* in about 10—20 minutes. The amount which Chapman observe and which ought to have been of the same order of magnitude wa reached in *ca.* 100 minutes of uninterrupted illumination. Therefor *their velocity was approximately 5—10 times smaller than* Lütke meyer's. Chapman and Briers worked at 191° (the b. p. of dimethyl *aniline) and* Lütkemeyer at *218°*. This difference of temperatur gives rise to a factor 3. The ratio thus corrected is due to th *difference in concentration of the bromine atoms.* Thus thi amounts, in the case of Chapman to about $\frac{3}{5}$—$\frac{3}{10}$ of that of Bodenstei and Lütkemeyer, where it is equal to $5{\cdot}5 \times 10^{-11}$ mole of bromin atoms per c.c. So in Chapman's work this is from $3{\cdot}3 \times 10^{-11}$ t $1{\cdot}65 \times 10^{-11}$ mole/c.c. *A quite similar value is obtained also* if th data of Chapman and Briers on the lamp and optical arrangement and so the energy absorbed, be taken into account, and the con centration of atoms calculated. Thus the mean life will be

$$\tau_1 = \frac{1}{C_1 A} = \frac{1}{C_1[\mathrm{Br}]} \sim \frac{1}{1{\cdot}55 \times 10^{11} \times (1{\cdot}65 \text{ to } 3{\cdot}3) \times 10^{-11}}$$

or $$\tau_1 \sim 0{\cdot}4 \text{ to } 0{\cdot}2 \text{ sec.}$$

If now τ_2 corresponds approximately to the *time which is necessar* for a bromine atom to diffuse from within the flask to the walls, the the average distance from the walls being about 1 cm., and th diffusion constant of bromine atoms being of the order of magnitud of 1 cm.^{2} sec.$^{-1}$, we have

$$\tau_1 \sim \frac{(\Delta x)^2}{2D} \sim 0{\cdot}5 \text{ sec.}$$

τ_2 would be still smaller if convection were taken into account. Thu for $A = 1$ *

$$C_1 : C_2 = 1/\tau_1 : 1/\tau_2 \sim (2{\cdot}5 \text{ to } 5) : 2$$

while Briers and Chapman (using the notation k_1 and k_2, which w have used *in another sense*) found

$$C_1 : C_2 = 0{\cdot}63 : 0{\cdot}37 \sim 3{\cdot}4 : 2$$

* The mean life is defined according to Briers and Chapman by $A = 1$ (their units).

Thus we obtain a good agreement. For the mean life, from $1/\tau = 1/\tau_1 + 1/\tau_2$, we have $\tau = 0{\cdot}14$—$0{\cdot}22$ sec., which, in view of the uncertainty of some of the underlying data, is in satisfactory agreement with the value found by Briers and Chapman, *viz.*, $\tau = 0{\cdot}063$ sec.

Our work agrees, then, with that of Briers and Chapman as well as the accuracy of the underlying data will permit. Furthermore, it leads distinctly to the fact that all measurements and theory must be based on bromine atoms and not on the excited molecules. That the thermal reaction between hydrogen and bromine to form hydrogen bromide goes through bromine atoms was shown independently by Christiansen (*Dansk. Vid. Math. Phys. Medd.*, 1919, **1**, 14), Herzfeld (*Z. Elektrochem.*, 1919, **25**, 301; *Ann. Physik*, 1919, **59**, 635), and Pólányi (*Z. Elektrochem.*, 1920, **26**, 50), who arrived at these conclusions from the measurements of Bodenstein and Lind (*Z. physikal. Chem.*, 1906, **57**, 168) on the dark reaction. The investigation of Bodenstein and Lütkemeyer showed, then, the same result for the light reaction, and that is through this work fully verified and extended in the manner described.

A quite analogous theory explains, of course, the work of Chapman and Grigg (J., 1928, 3233) on the influence of the wall on the combination of hydrogen and chlorine in light, though here the lack of numerical data makes the work only of a qualitative nature.

BERLIN, PHYSIKALISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT.
HANNOVER, ELECTROCHEMISCHES INSTITUT DER TECHNISCHEN HOCHSCHULE.
GREIFSWALD, CHEMISCHES UNIVERSITÄTS-LABORATORIUM.

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CLIV.—*Photochemical Equilibrium in Nitrogen Peroxide. Part II. The Dependence of Quantum Efficiency on Wave-length.*

By RONALD G. W. NORRISH.

IT has been shown (J., 1927, 761) that nitrogen peroxide exposed to the light of the mercury-vapour lamp undergoes a perfectly reversible decomposition and reaches a state of photochemical equilibrium represented by the equation

$$2NO_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} 2NO + O_2.$$

This involves an increase of pressure in the system while under

illumination, and the magnitude of this increase was found to be in agreement with the hypothesis that the reaction occurs as the result of a collision between a photoactive and an inactive molecule of peroxide, whilst the reverse " dark " reaction takes place according to a termolecular law, as shown by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 87). These general conclusions have been confirmed by Dickinson and Baxter (*J. Amer. Chem. Soc.*, *1928*, **50**, *774), who, by a different method, have studied the reaction at a lower pressure range, where the reverse dark reaction is insignificant. By freezing out the residual nitrogen peroxide and the nitric oxide produced, these authors were able to measure the extent of the light reaction from the oxygen formed, and to determine its quantum efficiency for the series of wave-lengths 436, 405, and 365* $\mu\mu$. Their results demonstrated the existence of a sharp photochemical threshold in the blue part of the spectrum, as will be seen from their mean figures for the quantum efficiency referred to nitrogen peroxide decomposed :

λ	436	405	365
γ	0·0092	0·72	1·54

Part of the work now described was in hand at the time of Dickinson and Baxter's publication, but in view of the importance of their results it has been delayed for a more extensive study of the relationship between quantum efficiency and wave-length. This has been carried out by a static method differing in principle from that employed by those authors, whose observation of a photochemical threshold existing well within the region of high absorption has been confirmed. The present indications are, indeed, that this photochemical threshold is sharper than originally supposed by Dickinson and Baxter, for, contrary to their result, it has been established that blue light of wave-length 436 $\mu\mu$ is without perceptible photochemical effect, the quantum efficiency being certainly less than 0·001.

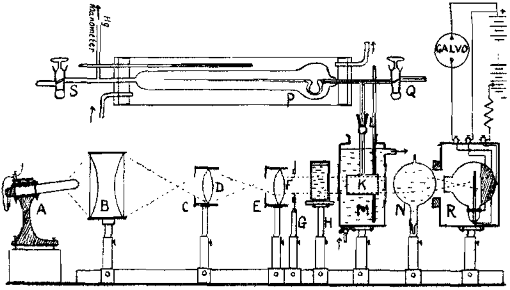
The principle of the method of measurement was to determine the pressure increase in the system when a photochemical stationary state had become established under the influence of monochromatic light of known intensity, and thence, from a knowledge of the velocity coefficient of the reverse dark reaction, to compare the number of quanta absorbed with the number of molecules of nitrogen peroxide decomposing in unit time. The results obtained indicate this as the first known case of a photochemical reaction showing a sharply developed threshold in the middle of a region of strong absorption, and yield data of considerable importance for the comparison of thermal and photochemical reactions (see Part III).

Experimental.

The apparatus * designed for this work (see Fig. 1) aimed at rapid and accurate measurements of light intensity and pressure change; and at the production of monochromatic light of various wave-lengths of sufficiently high intensity to bring about easily measurable photochemical change.

The mercury-vapour lamp A, lens system, and reaction vessel were fixed permanently on an accurate optical bench. The maximum quantity of light from the lamp was collected by the large condensing lens B, and concentrated to a parallel beam by the lenses D and F, the field being limited by the variable iris-diaphragm stops

FIG. 1.



C and E, before entering the reaction chamber K. A shutter G, worked from a distance by a pneumatic control, permitted illumination of the reaction vessel at will. The lenses were arranged for parallel light as intense as possible to pass through the reaction chamber. When it was later desired to use light of wave-length shorter than 365 $\mu\mu$, which is absorbed by glass, this lens system was replaced by quartz flasks containing a solution of the colour filter. By using a large flask as the condenser, in conjunction with a smaller flask, a convergent, sharply defined beam was obtained, which proved as satisfactory in all respects as the beams of longer wave-length obtained with the glass lenses.

The mercury lamp was of the horizontal U-type made by the

* The grateful acknowledgment of the author is due to Mr. H. M. Roberts, in collaboration with whom this apparatus was originally set up for another purpose.

Hewittic Company, and was worked from a 220-volt supply furnished by storage batteries. The burner voltage was 150 volts and the current 2·25 amps., and under these conditions a light emission of very constant intensity was obtained.

The reaction chamber itself consisted of a cylindrical quartz vessel, of length 4 cm. and diameter 3 cm., with parallel, plane, quartz end-plates fused on. It was mounted axially with the lens system, and was connected by a capillary tube and a ground-glass joint L to the Bourdon gauge P (see Part I, *loc. cit.*) and to the nitrogen peroxide supply and pumps *via* tap Q. The temperatures of the reaction vessel aud gauge were controlled to 25° ± 0·01° by pumping water from an electrically controlled thermostat to a cistern with a constant-level regulator, fixed above the apparatus, and allowing the water to run back to the thermostat through (1) an external jacket surrounding the gauge, and (2) a rectangular tank, M, with plane plate quartz faces, mounted axially on the optical bench as a thermostat for the reaction vessel. By this means it was possible to control the temperature of both gauge and reaction vessel to ± 0·01° for as long as desired, only occasional slight adjustment of the speed of water flow being necessary.

The pressure changes in the system could be measured very accurately by following the movement of the gauge pointer with a travelling microscope mounted in front of the apparatus. The microscope could be set accurately to 0·005 mm., and it was found that the deflexion of the gauge varied in a linear manner with pressure for small deflexions. The gauge was calibrated by measuring small pressure differences between its inside and outside directly on vertical mercury manometers, using a travelling telescope; and it was found that a deflexion of the gauge pointer by 1 mm. corresponded to a pressure change of 7·00 mm., the probable error in the determination of a pressure change of the order of 2 mm. being not greater than 2%.

The arrangements for evacuating the apparatus and filling it with nitrogen peroxide or other desired gas were exactly as stated in Part I (*loc. cit.*). The nitrogen peroxide was prepared and purified as there described.

Colour Filters.—In order to obtain monochromatic light beams of sufficient strength and purity the following colour filters were mounted on the stage H in the path of the light, immediately in front of the reaction vessel tank.

(1) Yellow at 575 μμ : Wratten mercury monochromat filter.

(2) Green at 546 μμ : Wratten mercury monochromat filter.

(3) Blue at 436 μμ : 3 Cm. layer of 1% solution of aqueous tetramminocopper sulphate (Vanino, "Präparative Chemie," 1921

I, p. 500), combined with ½ cm. layer of 6% aqueous quinine hydrochloride solution.

(4) *Violet at 405 μμ: 3 Cm. layer of 0·02N-iodine* in carbon tetrachloride solution, combined with ½ cm. layer of 0·1% aqueous quinine hydrochloride solution.

(5) Ultra-violet at 365 μμ : Wratten mercury monochromat filter.

(6) Ultra-violet at 316—270 μμ : 7% Nickel chloride hexahydrate in aqueous solution contained in quartz flasks used as lenses of total thickness about 20 cm. This filter also transmits green light, but as this affects neither the nitrogen peroxide decomposition nor the sodium photoelectric cell used to measure the intensity of the ultra-violet light, it can be neglected.

Measurement of Light Intensity.—Measurements of light intensity and light absorption were made by a gas-filled sodium photoelectric cell with a quartz window, which was satisfactorily sensitive over the spectrum range λλ 450—250 μμ. The cell, fixed in a light-proof box with a shutter, was mounted on the optical bench at R, the light emerging from the reaction vessel being brought to a sharp focus in the cell hy means of a spherical quartz globe, N, filled with water and mounted axially in the system. The photoelectric current generated was measured by a sensitive moving-coil mirror galvanometer.

The photoelectric cell can only be used to measure the absolute intensity of light of a given wave-length after calibration by a thermopile for that particular wave-length. These calibrations were made for the separate wave-length regions of the mercury-vapour lamp at 436, 405, 365, and 316—270 μμ by the help of a Moll thermopile which had been previously calibrated for energy radiation by means of a Leslie cube. The procedure adopted is described below:

(1) *Calibration of thermopile.* The thermopile was used in conjunction with a Broca galvanometer of about 100 ohms resistance, deflexions being measured with a lamp and scale at 1 metre distance. The Leslie cube contained water maintained at 100° by means of an internal electric heater. The dimensions of the black face of the cube were 10 × 10 cm., and the diameter of the face of the thermopile which was used without its funnel was 1·36 cm.

The thermopile was mounted in front of the Leslie cube at distances of 1 and 1½ metres, and screened from its rays by a photographic shutter which could be actuated from a distance. With the temperature of the air at 19°, the following mean galvanometer deflexions were obtained with the thermopile :

(*a*) Cube at 1 metre : mean deflexion 3·16 cm.
(*b*) Cube at 1½ metres : mean deflexion 1·44 cm.

The readings did not vary by more than 1 mm. amongst themselves. Since $150^2/100^2 = 2{\cdot}25$ and $3{\cdot}16/1{\cdot}44 = 2{\cdot}20$, it will be seen that the law of inverse squares is approximately obeyed.* From these figures, allowing for the fact that the total radiation from the cube is only 90% of the theoretical (Poynting and Thomson, "Heat," 5th edtn., 1919, p. 321), we calculate that 1 cm. galvanometer deflexion corresponds to a total flux of 460 ergs per second on to the thermopile.

(2) *Calibration of photoelectric cell.* The following procedure relates to the calibration for the lines 436, 405, and 365 $\mu\mu$. First the thermopile and secondly the photoelectric cell were mounted at R (Fig. 1) and arranged so that their sensitive surfaces received the whole of the light field, concentrated by the quartz-water lens N. The appropriate colour filters were mounted at A, in combination with a filter of 6% aqueous solution of copper sulphate 3 cm. thick to remove infra-red radiation. The deflexions of the galvanometers attached to the thermopile and cell were compared, the mean values calculated from 20 observations in each case being recorded in Table I (*a*). The calibrations for the various wave-lengths were then calculated for the photoelectric cell, and are shown in the last two columns in ergs and quanta per second.

TABLE I.

(*a*) (Calibration for thermopile : 1 cm. galvo. deflexion ≡ 460 ergs/sec.).

Wave-length ($\mu\mu$) or spectral region.	Mean thermopile reading (Broca galvo.).	Mean photoelectric reading (moving-coil galvo.).	1 Cm. deflexion of second galvanometer corresponds to ergs/sec.	quanta/sec.
436	5·80 cm.	9·10 cm.	293	$6{\cdot}5 \times 10^{13}$
405	3·32	9·02	170	$3{\cdot}51 \times 10^{13}$
365	3·60	21·08	78·9	$1{\cdot}46 \times 10^{13}$

(*b*) (Calibration for thermopile : 1 cm. galvo. deflexion ≡ 1360 ergs/sec.).

Passed by $NiCl_2$ filter alone	8·4	40·2	—	—
Passed by $NiCl_2$ + glass plate	4·3 + 9%	2·9 + 9%	—	—
316—270 $\mu\mu$ *	3·7	37	136	$2{\cdot}0 \times 10^{13}$

* Mean value of $h\nu = 6{\cdot}8 \times 10^{-12}$ erg.

A separate calibration for the spectral region 316—270 $\mu\mu$ wa made in the following way : A different setting of the Broca galvano meter gave a sensitivity corresponding to 1360 ergs per sec. per cm deflexion for the thermopile. The light passing the nickel chlorid filter consisted almost entirely of the mercury green light, and th

* The geometrical deviation from the simple inverse-square law due to th extended surface of the source is easily shown to be not greater than 0·3% a distance of 1 metre.

ultra-violet light of wave-length region 316—270 μμ, the latter being almost completely absorbable by a glass plate. Two sets of readings of the thermopile and photoelectric cell were therefore taken, (1) through glass, and (2) with the light falling direct. The difference of these two sets of readings, allowance being made for a 9% reflexion by the glass plate, gives the effect corresponding to the ultra-violet light alone.

No copper sulphate filter for infra-red was needed in this case, since the nickel chloride itself acts effectively in this respect, and in any case the differential method of calibration used would automatically correct for any infra-red effect if it existed. From the results of this calibration (Table I *b*) it will be seen that over 92% of the ultra-violet radiation transmitted by this filter is absorbable by glass, a result which conclusively demonstrates the absence of any appreciable quantity of the longer wave-length ultra-violet light at 365 μμ. The total absence of all light between the green at 546 μμ and the ultra-violet at 336 μμ has been further proved by a series of absorption photographs of the nickel chloride filter, and there is every reason to believe that the residual photoelectric effect through glass is due to the slight transmission of the shorter ultra-violet light between 316 and 270 μμ. This being so, and since green light has no effect on the photoelectric cell, we may take the photoelectric galvanometer deflexion as a measure solely of the ultra-violet light in the beam.

The Measurement of Quantum Efficiency.—The measurement of quantum efficiency was made for wave-lengths ranging from the yellow to the ultra-violet by filling the reaction vessel with nitrogen peroxide at any desired pressure, and exposing it to the monochromatic radiation until the system had come to a photochemical stationary state, the oxygen produced in the reaction being calculated from the increase in pressure. The amount of light absorbed by the system was determined simultaneously in terms of quanta by the photoelectric cell, by observing its deflexions with the reaction vessel (1) filled with the nitrogen peroxide and (2) evacuated. From the pressure of oxygen produced, we may calculate the speed of its recombination with the nitric oxide at equilibrium (Bodenstein and Lindner, *Z. physikal. Chem.*, 1922, **100**, 87) and hence the equal rate of decomposition of nitrogen peroxide. From this, a knowledge of the dimensions of the apparatus gives the number of molecules breaking up photochemically per second, and the quantum sensitivity.

Special attention was paid to the following precautions and corrections:

(*a*) Removal of all excess oxygen from the system before filling with nitrogen peroxide in order to obviate suppression of the photo-

chemical equilibrium : this was done by continued pumping out and washing with pure nitrogen.

(*b*) The heating effect of the recombination of the nitric oxide and oxygen, which, as shown in Part I, may cause a pressure increase : in the present case, however, this was negligible, for with the comparatively low intensities of light used, and the correspondingly smaller degree of photodecomposition, no measurable residual heating effect was observable on adding excess of nitric oxide.

(*c*) The loss of light by reflexion after leaving the reaction vessel, and before reaching the radiometer : the light, after entering the reaction cell, has to pass four quartz faces, *viz.*, the back faces of the cell and thermostat and the two faces of the water lens, before it is measured by the radiometer. The measured intensity must therefore be corrected for light lost by reflexion at these faces. Taking the refractive index of the quartz as 1·47 (value for fused silica), we may calculate that each water–quartz surface reflects 0·2% of the incident light, and each gas–quartz surface 3·6%. Since there are four surfaces of each type, the measured intensity must be multiplied by the factor 1·17 to obtain the true intensity of the light leaving the reaction vessel.

(*d*) The accurate determination of the volume of the reaction cell and gauge : this was effected by filling the reaction system with air at atmospheric pressure and a known temperature, evacuating it completely by means of a Toepler pump, and measuring the volume of the air pumped out. In this way the volume of the reaction system, cell and gauge was found to be 30·3 c.c.

(*e*) The calculation of the pressures of oxygen and nitric oxide produced at equilibrium : the increase of pressure at photochemical equilibrium must be corrected for the change in dissociation of the N_2O_4 in order to obtain the true pressure of oxygen produced in the reaction $2NO_2 \rightleftharpoons 2NO + O_2$. This was done as follows : If P and P_0 represent respectively the initial total pressure of nitrogen peroxide (*i.e.*, N_2O_4 and NO_2) and partial pressure of NO_2, and P' and P'_0 have the same significance when photochemical equilibrium has been reached, we have at 25°, by the relationship of Wourtzel (*Compt. rend.*, 1919, **169**, 1397),

$$P_0^2/(P - P_0) = P'^2_0/(P' - P'_0) = 108 \quad . \quad . \quad . \quad (1)$$

Further, if x represents the true pressure of oxygen produced, and $2x$ that of the nitric oxide, the observed pressure increase p is given by

$$p = (P' + 3x) - P \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Finally, representing all the nitrogen peroxide in terms of NO_2, we have for the initial quantity $(2P - P_0)$, and for the quantity

present at photochemical equilibrium ($2P' - P'_0$). These amounts differ by $2x$ the pressure of NO_2 decomposed ; hence

$$2P' - P'_0 = 2P - P_0 - 2x \quad . \quad . \quad . \quad . \quad (3)$$

Eliminating P_0, P', and P'_0 from equations (1), (2), and (3), we obtain

$$x^2 - (p + \sqrt{27P + 730} - 20{\cdot}25)x + p\left(\frac{p}{4} + \tfrac{1}{2}\sqrt{27P + 730} - 6{\cdot}75\right) = 0 \quad . \quad . \quad (4)$$

and since P and p are known, this may be solved for x, the equilibrium pressure of oxygen.

Calculation of the Quantum Efficiency.—At photochemical equilibrium the number of molecules of nitric oxide and oxygen recombining per second is known from the value of x (as obtained above), the volume of the vessel, and the velocity coefficient of the reaction determined by Bodenstein and Lindner (*loc. cit.*). Thus, at 25°

$$d[2NO_2]/dt = 1{\cdot}66 \times 10^6 \times [2NO]^2[O_2]$$

the concentrations being measured in mols. per litre and the time in minutes. The equilibrium pressure of oxygen is x; hence, in the present instance

$$[2NO] = \tfrac{1}{2}[NO] = [O_2] = x\left(\frac{1}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)$$

The number of mols. of NO_2 decomposed per litre per second is therefore

$$-\frac{d[NO_2]}{dt} = -2\frac{d[2NO_2]}{dt} = 2\left(\frac{x}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)^3 \times \frac{1{\cdot}66}{60} \times 10^6.$$

Taking the volume of the cell as 30·3 c.c. and the Avogadro number as $6{\cdot}06 \times 10^{23}$, we find for the number of molecules decomposed per second

$$n = 2\left(\frac{x}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)^3 \times \frac{1{\cdot}66 \cdot 10^6}{60} \times \frac{6{\cdot}06 \cdot 10^{23} \cdot 30{\cdot}3}{1000}$$
$$= 1{\cdot}587 \times 10^{14} \times x^3.$$

If A represents the light absorbed by the NO_2, measured in terms of galvanometer deflexion, the number of quanta absorbed per second is $m = 1{\cdot}17Af$, where f represents the appropriate factor (see Table I) for converting the galvanometer deflexion into quanta per second, and the factor 1·17 corrects for loss of light by reflexion (see above). The quantum efficiency is then given by

$$\gamma = n/m = 1{\cdot}587 \times 10^{14}x^3/1{\cdot}17Af = 1{\cdot}36 \times 10^{14}x^3/Af.$$

The experimental results and the values of the quantum efficiency calculated from them are shown for various wave-lengths in Tables II

and III. The light intensities for Table II were measured by the thermopile, and those for Table III by the photoelectric cell, the appropriate values of the factor f (from Table I) being shown in the latter case.

TABLE II.

Wave-lengths 575 and 540 $\mu\mu$.

Wave-length, $\mu\mu$.	Pressure of NO_2.	Energy of beam (cals./sec.).	Energy absorbed, %.	Pressure increase in NO_2 (mm.).	γ.
575	223	$1{\cdot}0 \times 10^{-4}$	Slight	0·00	0·000
546	32	$1{\cdot}2 \times 10^{-4}$	39	0·13	0·000
546	150	$1{\cdot}2 \times 10^{-4}$	70	0·07	0·000
546	190	$1{\cdot}2 \times 10^{-4}$	80	0·15	0·000

TABLE III.

Initial press. of NO_2, mm.	Intensities (galvo. deflexion). Incident.	Transmitted.	Absorbed.	Press. increase, mm.	x.	γ.
	(a) Wave-length 436 $\mu\mu$; $f = 6{\cdot}5 \times 10^{13}$.					
10	7·1	3·0	4·1	0·00	0·00	0·000
56	11·7	1·0	10·7	0·00	0·00	0·000
100	12·9	0·3	12·6	0·00	0·00	0·000
150	11·9	0·0	11·9	0·08	0·06	0·000
	(b) Wave-length 405 $\mu\mu$; $f = 3{\cdot}51 \times 10^{13}$.					
22	15·6	3·7	11·9	1·79	1·28	0·68
25	10·2	2·4	7·8	1·71	1·20	0·85
56	10·0	0·8	9·2	1·92	1·20	0·72
100	10·2	0·3	9·9	2·06	1·22	0·72
265	11·3	0·0	11·3	2·35	1·29	0·74
					Mean	0·74
	(c) Wave-length 365 $\mu\mu$; $f = 1{\cdot}46 \times 10^{13}$.					
22	54·0	17·0	37·0	2·87	2·06	2·18
25	22·6	7·3	15·3	2·17	1·52	2·13
56	19·0	1·2	17·8	2·56	1·60	2·14
100	21·8	0·3	21·5	2·85	1·69	2·07
268	27·0	0·0	27·0	3·26	1·79	1·98
					Mean	2·10
	(d) Wave-length 316—270 $\mu\mu$; $f = 2{\cdot}0 \times 10^{13}$.					
22	35·8	23·0	12·8	2·23	1·59	2·13
30	16·1	7·5	8·6	2·03	1·38	2·07
48	30·5	15·7	24·8	3·05	1·95	2·03
105	33·5	1·5	32·0	3·50	2·06	1·87
213	31·3	0·0	31·3	4·05	2·26	2·45
					Mean	2·07

The data of Table III (a) indicate no detectable photochemical effect for blue light of 436 $\mu\mu$. This is contrary to the observation of Dickinson and Baxter, who reported a quantum efficiency of 0·0092, a magnitude well within the scope of the present apparatus. For example, light absorption corresponding to 11 galvanometer

scale divisions would involve a value of x of about 0·4 mm. and a total pressure change of the order 0·5—0·7 mm., whilst, as stated above, pressure changes of the order 0·05 mm. could be easily detected. It would therefore appear that the blue colour filter employed by Dickinson and Baxter was somewhat inefficient and slightly transparent to ultra-violet or violet radiation.

The results given in Tables II and III raise certain issues of importance to the theory of photochemical change. The existence of a sharp photochemical threshold between wave-lengths 436 and 405 $\mu\mu$ in a region of high absorption suggests the inquiry as to what happens to the absorbed energy of the former wave-length. The quantum involved, 64,000 cals. per g.-mol., is at least double the magnitude of energy required in the corresponding homogeneous bimolecular thermal reaction, where the energy of activation is about 33,000 cals. per [$2NO_2$] and the heat of reaction 26,000 cals. (Bodenstein and Lindner, *loc. cit.*; Norrish, *Nature*, 1928, **122**, 923); and yet this quantity of energy is absorbed without chemical effect. Again, to what cause must one attribute the partial efficiency of violet light which introduces ample energy into the molecule for bimolecular decomposition? It is clear that only a part of the absorbed energy is available for chemical change, and that certain probability considerations affect its utilisation.

The fact that with further increase of wave-length the quantum efficiency reaches a maximum constant value of 2 indicates that the probability factor soon reaches unity, and demonstrates the absence of any chain reaction. In this respect the present finding confirms the collision hypothesis advanced in Part I (*loc. cit.*), and makes possible a comparison on equal terms of the homogeneous photochemical and thermal decompositions of nitrogen peroxide.

The points raised above will be considered at greater length in Part III.

Summary.

The quantum efficiency (γ) of the photochemical reaction $2NO_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} 2NO + O_2$ has been investigated for six wave-lengths of the mercury-vapour lamp in the visible and ultra-violet, a photoelectric cell being used to measure light intensity. The following values were obtained: for 575, 546, 436 $\mu\mu$, $\gamma = 0·000$; for 405 $\mu\mu$, $\gamma = 0·74$; for 365 $\mu\mu$, $\gamma = 2·10$; and for 316—265 $\mu\mu$, $\gamma = 2·07$. The photochemical threshold in the middle of the nitrogen peroxide absorption region noticed by Dickinson and Baxter has been found to be sharper than was originally supposed, their observation of slight photochemical activity of light of λ 436 $\mu\mu$ being definitely

unconfirmed. No difference could be observed between the quantum efficiency of light of λ 365 and λ 316 μμ; the values obtained indicated complete efficiency. The existence of fine structure in the NO_2 absorption spectrum is in agreement with the mechanism $NO_2 + h\nu = NO_2'$; $NO_2 + NO_2' = 2NO + O_2$, which is also confirmed by the kinetic observations in Part I.

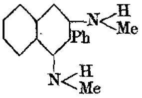
The thanks of the author are due to the Royal Society for a grant towards the cost of apparatus which has made this work possible.

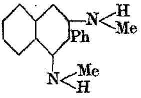
DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, February* 26*th*, 1929.]

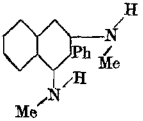
CLV.—N-*Methyl Derivatives of 2-Phenylnaphthylene-1 : 3-diamine.*

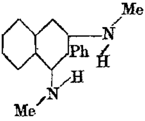
By WILLIAM SIMPSON KENTISH.

THE isomerism of the α- and β-*NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamines, examined by Lees and Thorpe (J., 1907, **91**, 1282) and by Gibson, Kentish, and Simonsen (J., 1928, 2131), can be explained by assuming either definite structural differences between the two isomerides or an interlocking of the phenyl and methyl groups producing *cis-trans* isomerism. On the latter assumption, the molecules of the isomeric dimethyl compounds may be either planar (I and II) or non-planar (III and IV).

(I.) 

 (II.)

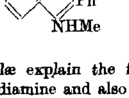
(III.) 

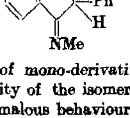
 (IV.)

The planar model was suggested by Gibson, Kentish, and Simonsen (*loc. cit.*, p. 2133), but there is much evidence against it. In the first place, there is no reason why the methylamino- and phenyl groups should remain in the plane of the ring, since they are rotating continuously and are not fixed as the assumption demands. Moreover, molecular models show that there is not sufficient space for the methyl groups to exist between the nitrogen atoms and the benzene

ring. In addition, only two of the four possible isomerides are known. The *non-planar model* assumes that the phenyl and methylamino-gronps interlock and that the former vibrates slightly about the plane of the naphthalene ring, the latter oscillating in planes perpendicular to that of the naphthalene ring. The formation of mono-derivatives of the *cis*- or α-dimethyldiamine (III) is explained if it is assumed that steric hindrance prevents two large substituents from entering the naphthalene ring on the same side. The failure to resolve either of the isomerides cannot be explained by assuming racemisation, because, in that event, the two isomerides themselves should be similarly interconvertible. Both models fail to explain adequately why the α-dimethyldiamine forms only mono-derivatives, since the trimethyldiamine can be readily acetylated and the dimethyldiamines pass very quickly into the tetramethyl compound when heated with methyl sulphate. Also, there is no explanation of the transformation in the presence of nitrous acid (see p. 1171), and why two nitroso-gronps can be introduced into the α-dimethyldiamine even though the nitroso- and the methyl group have comparable molecular volumes. There is no reason why the isomerides should not he interconvertible in the presence of strong reagents, as the molecular model shows that the overlapping of groups is not so great as that observed in the case of the enantiomorphic forms of 2 : 6 : 2′-trisubstituted diphenyl eompounds (Kenner and others, J., 1922, **121**, 614, etc.; Mills, *Chem. and Ind.*, 1926, **45**, 883) and the disubstituted 1 : 8-nitronaphthylamines (Mills and Elliott, J., 1928, 1291) and also of the exactly comparable isomerides of 5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid (Hayashi, J., 1927, 2516; compare Kentish, *Chem. and Ind.*, 1928, **47**, 952), and yet these are readily interconvertible.

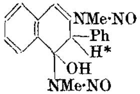
In the light of this evidence, more attention may be given to the *structural explanation of the isomerism*. Of the many possibilities, the most probable represents the β-form as the simple dimethylnaphthylenediamine (V) and the α-form as a methylimino-compound with a reduced naphthalene ring (VI).

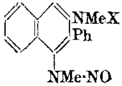
(V.) 

 (VI.)

The formulæ explain the formation of mono-derivatives of the α-dimethyldiamine and also the stability of the isomerides in the presence of strong reagents. The anomalous behaviour of nitrous acid, which rapidly transforms the α-dimethyldiamine into the β-dinitrosoamine (very slow transformation in the case of acetic

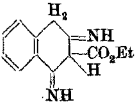
anhydride and other reagents is not, however, excluded), is probably due to the addition of the reagent at the methylimino double bond giving the compound (VII) and the elimination of the hydroxyl group and the hydrogen atom (marked *) as water, giving the β-dinitrosoamine (VIII; X = NO).

(VII.) 

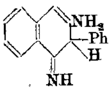
 (VIII.)

Owing to the intractability of the salts of the dimethyldiamines and optically active acids, the evidence for non-resolvability lies largely in the homogeneity of the methylenecamphor derivatives. Since, however, several cases have already been found where this reagent has not effected resolution, the evidence for non-resolvability cannot be accepted as definitely established. In the case of the β-dimethyldiamine, rapid racemisation would indeed be expected.

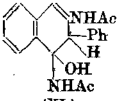
Atkinson and Thorpe (J., 1906, **89**, 1906) considered that ethyl 1 : 3-diaminonaphthalene-2-carboxylate had the di-imino structure (IX), as it had a yellow colour, and that the corresponding carboxylic acid together with 2-phenylnaphthylene-1 : 3-diamine and naphthylene-1 : 3-diamine, being colourless, had the diamino structure. It is, however, very probable that 2-phenylnaphthylene-1 : 3-diamine has the mono-imino structure (X), because the 1-amino-group cannot be diazotised unless there is an acetyl group in the 3-position. Finally, on acetylation of the diamine with acetic anhydride, an "acetyl acetate" is obtained (Atkinson and Thorpe, *loc. cit.*). This is not a true salt, as, on treatment with caustic soda, it passes immediately into the diacetyl compound. It is evident that, during acetylation, acetic acid adds on at the imino double bond, giving the compound (XI) analogous to that obtained with nitrous acid. Loss of water occurs in this case only in the presence of alkalis. The isolation of the intermediate compound undoubtedly strongly supports the imino structure of 2-phenylnaphthylene-1 : 3-diamine.



(IX.)



(X.)

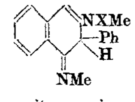


(XI.)

When 2-phenylnaphthylene-1 : 3-diamine is methylated with methyl sulphate and alkali in the cold, the imino structure is retained in the

case of the α-dimethyldiamine; transformation, however, takes place *on further methylation, since the tetramethyldiamine is also* obtained (compare the amino structure of 3-acetyl-2-phenylnaphthylene-1 : 3-diamine). When the diamine is heated with methyl sulphate, transformation occurs and the β-dimethyldiamine is obtained. The transformation is probably due to the addition of methyl sulphate (Me and $MeSO_4$ being the two addenda) at the imino double bond and the subsequent splitting off of the $MeSO_4$ and H groups. This addition may only occur under the conditions of the second method of methylation, as alkalis would tend to retain the $MeSO_4$ addendum.

It seemed to be of considerable interest to examine the mechanism of the action of nitrous acid in converting the α- into the β-dimethyldiamine. The only method of effecting an interchange was described by Gibson, Kentish, and Simonsen (*loc. cit.*) and involved the action of nitrous acid on the α-dimethyldiamine, giving the β-dinitrosoamine, and the subsequent reduction of this to the β-dimethyldiamine. The slowness of the action of nitrous acid on the α-dimethyldiamine in comparison with the normal rate of acetylation, etc., of this base suggests that the acid-soluble α-mononitrosoamine is produced immediately and is slowly transformed into the β-dinitrosoamine. When the α-dimethyldiamine is treated with one molecule of nitrous acid, a good yield of α-3-*nitrosomethylamino-1-methylimino-2-phenyl-1 : 2-dihydronaphthalene* (XII; X = NO) is obtained. This is dimorphic like many other compounds of this series. Evidently some peculiarity in the structure presents an alternative method of packing the molecules in the crystals.

(XII.) 

(XIII.)

As this mononitrosoamine can be reduced to the α-dimethyldiamine, and also slowly converted into the β-dinitrosoamine when treated with nitrous acid, it is evident that the transformation occurs when the second nitroso-group is introduced. The α-mononitrosoamine can be neither methylated nor condensed with *p*-toluenesulphonyl chloride. In order to discover whether the transformation was in any way specifically associated with the first nitroso-group, the action of nitrous acid on the monoacetyl and mono-*p*-toluenesulphonyl derivatives of the α-dimethyldiamine was investigated. The α-monoacetyl compound (XII; X = $CO{\cdot}CH_3$) gave a *nitrosoamine* (VIII; X = $CO{\cdot}CH_3$) fairly quickly, and this was reduced to a new acetyl compound which could be hydrolysed to the β-dimethyl-

diamine and was therefore β-3-*acetylmethylamino*-1-*methylamino*-2-*phenylnaphthalene* (XIII; X = $CO{\cdot}CH_3$).

The α-mono-*p*-toluenesulphonyl compound (XII; X = $SO_2{\cdot}C_7H_7$) similarly gave a *mononitrosoamine* (VIII; X = $SO_2{\cdot}C_7H_7$) which gave the β-dimethyldiamine after removal of the nitroso- and *p*-toluenesulphonyl groups.

The transformation is thus seen to be unassociated with the nature of the first substituent in the α-dimethyldiamine, and evidence seems now to have accumulated to show that nitrous acid effects a definite structural transformation.

Further support for the structural explanation of the isomerism of the dimethyldiamines was obtained by the preparation of the mononitrosoamine of the β-dimethyldiamine. When the latter was treated with one molecule of nitrous acid, the greater part of the product obtained consisted of the dinitrosoamine and unchanged base, but a small quantity of the β-*mononitrosoamine* (XIII; X = NO) was also isolated with some difficulty.

The β-mononitrosoamine had a deep red colour and gave intensely coloured solutions, whereas solutions of the α-mononitrosoamine were only slightly coloured. The intensity of colour in the former compound would be expected, as there is a chromophore (N·NO) and an auxochrome (NHMe) present as substituents in a phenylnaphthalene ring. In the α-mononitrosoamine, the naphthalene ring is absent.

It is proposed to see whether absorption spectra will furnish proof of the structure of the derivatives of 2-phenylnaphthylene-1 : 3-diamine.

EXPERIMENTAL.

α-3-*Nitrosomethylamino*-1-*methylimino*-2-*phenyl*-1 : 2-*dihydronaphthalene* (XII; X = NO).—α-*NN'*-Dimethyl-2-phenylnaphthylene-1 : 3-diamine (VI) (7 g.) was dissolved in 15% hydrochloric acid (70 c.c.), and sodium nitrite (1·95 g.) in aqueous solution (10 c.c.) added slowly with mechanical stirring at the ordinary temperature. After a few minutes, a slight precipitate of dinitrosoamine was filtered off and the filtrate was basified with ammonia. The red oil obtained quickly solidified (7·3 g.), and on crystallising from alcohol the α-*mononitrosoamine* was isolated in 70% yield (Found: N, 14·5. $C_{18}H_{17}ON_3$ requires N, 14·4%). It had m. p. 154° and was dimorphic; the unstable α_1-form separated first from solutions as a mass of fine yellow glistening needles and quickly passed into the glistening orange-red prisms of the stable α-form. Both had the same melting point. The mononitrosoamine gave the Liebermann reaction and was soluble only in fairly concentrated hydrochloric acid.

A solution of the mononitrosoamine (4 g.) in glacial acetic acid (60 c.c.) was heated with excess of tin and concentrated hydrochloric

acid (30 c.c.) on the water-bath for 20 minutes. Excess of solid caustic soda was added to the decanted liquid, and the solution boiled for a few minutes to decompose double salts of tin. The product was extracted with hot benzene and was worked up in the usual way. A nearly theoretical yield of the α-dimethyl base (VI) was obtained (m. p. 169° after crystallising from light petroleum, b. p. 60—80°).

The α-mononitrosoamine (1 g.) was dissolved in 20% hydrochloric acid (40 c.c.), and excess of sodium nitrite solution added. The β-dinitrosoamine (VIII; X = NO) separated slowly and had m. p. 179° after crystallising from alcohol.

When the α-mononitrosoamine was heated with *p*-toluenesulphonyl chloride in pyridine solution for 4 hours at 100°, and methylated with methyl sulphate and caustic soda in methyl-alcoholic solution in the usual way, it was recovered unchanged.

Action of Nitrous Acid on α-3-*Acetylmethylamino*-1-*methylimino*-2-*phenyl*-1 : 2-*dihydronaphthalene*.—The α-monoacetyl compound (XII; X = $CO{\cdot}CH_3$) (8 g.), dissolved in 10% hydrochloric acid (150 c.c.), was treated with a slight excess of sodium nitrite solution. After ½ hour, the precipitate was collected, washed with water, and crystallised from alcohol, in which it was readily soluble; β-3-*acetylmethylamino*-1-*nitrosomethylamino*-2-*phenylnaphthalene* (VIII; X = $CO{\cdot}CH_3$) separated in pale yellow lustrous plates, m. p. 198° (Found: N, 12·8. $C_{20}H_{19}O_2N_3$ requires N, 12·6%). It gave the Liebermann reaction.

The acetylnitrosoamine (4 g.) was dissolved in acetic acid (40 c.c.) and reduced with tin and hydrochloric acid, giving β-3-*acetylmethylamino*-1-*methylamino*-2-*phenylnaphthalene* (XIII; X = $CO{\cdot}CH_3$) (3 g.). This was very soluble in the ordinary solvents and crystallised from dilute alcohol in prisms, m. p. 147° (Found: N, 9·2. $C_{20}H_{20}ON_2$ requires N, 9·2%).

The β-monoacetyl compound was not appreciably hydrolysed by boiling with 40% caustic soda solution or alcoholic sulphuric acid. When it was refluxed for 4 hours with concentrated hydrochloric acid, and the product crystallised from alcohol, a good yield of the β-dimethyldiamine (V) (m. p. 158°) was obtained.

Action of Nitrous Acid on p-*Toluenesulphonyl*-α-*NN'*-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*.—The α-mono-*p*-toluenesulphonyl compound (XII; X = $SO_2{\cdot}C_7H_7$) (5 g.) was dissolved in concentrated hydrochloric acid (80 c.c.) and an equal volume of water was added, followed by a slight excess of sodium nitrite solution. A pale yellow precipitate formed fairly quickly, and after 30 minutes this was collected, washed with water, and crystallised from alcohol, in which it was fairly soluble; *nitroso*-p-*toluenesulphonyl*-β-*NN'*-

dimethyl-2-phenylnaphthylene-1 : 3-diamine (VIII; X = $SO_2 \cdot C_7H_7$) separated in pale yellow plates, m. p. 183°, which gave the Liebermann reaction (Found : N, 9·5. $C_{25}H_{23}O_3N_3S$ requires N, 9·4%).

The β-*nitroso*-p-*toluenesulphonyl compound* (3 g.) was reduced with tin and hydrochloric acid in acetic acid solution. The solid resin obtained was at once hydrolysed by heating at 120° with 20 c.c. of a mixture of glacial acetic acid (30 parts) and concentrated sulphuric acid (70 parts) until the whole had dissolved. On pouring the mixture into water and basifying it with ammonia, 1 g. of the β-dimethyldiamine (m. p. 159° after crystallising from alcohol) was obtained.

β-3-*Nitrosomethylamino*-1-*methylamino*-2-*phenylnaphthalene*.—The β-dimethyl base (7 g.), dissolved in 20% hydrochloric acid (100 c.c.), was treated with sodium nitrite (2·02 g.) in aqueous solution (10 c.c.) at 0°. After 15 minutes, the dinitrosoamine was filtered off; the filtrate, basified with ammonia, gave a deep red solid. This consisted mainly of the β-dimethyl base, which was removed by digesting the solid several times with 10% hydrochloric acid. The residue was basified with ammonia and crystallised from a mixture of 3 parts of alcohol and 1 part of benzene, the β-*mononitrosoamine* (XIII; X = NO) separating in minute, deep red needles with a violet fluorescence, m. p. 248° (Found: N, 14·6. $C_{18}H_{17}ON_3$ requires N, 14·4%). It was fairly readily soluble in alcohol and readily soluble in benzene, giving intensely coloured crimson solutions. The hydrochloride was yellow and rather sparingly soluble in water. Owing to the small amount of β-mononitrosoamine obtained in this reaction, it was not possible to prove the constitution by conversion either into the dinitrosoamine or into the β-dimethyldiamine; but it was not considered likely that the nitroso-group had entered the naphthalene ring, as no similar compound was obtained when excess of nitrous acid was used or when the α-dimethyldiamine was treated with nitrous acid.

Acetyl Acetate Derivative of 2-Phenylnaphthylene-1 : 3-diamine.—The acetyl acetate compound (XI) was dissolved in alcohol and treated in the cold with excess of 5% aqueous caustic soda, and the solution poured into water after a few minutes. The precipitate, m. p. 272°, was the pure diacetyl-2-phenylnaphthylene-1 : 3-diamine (Atkinson and Thorpe, J., 1906, 89, 1935, give m. p. 267°).

The author wishes to express his thanks to Professor W. N. Haworth, F.R.S., who kindly arranged to have the microanalysis of the β-mononitrosoamine carried out in his laboratories.

SPONDON, near DERBY. [*Received, April 8th, 1929.*]

CLVI.—*Organic Derivatives of Silicon. Part XXXIX. The Action of Sodium on Phenoxychlorosilicanes.*

By REGINALD AUBREY THOMPSON and FREDERIC STANLEY KIPPING.

A VERY few silicon compounds of the type SiR_3Cl are known to be converted into derivatives of silicoethane when they are heated with sodium (Kipping, J., 1921, **117**, 647), but diphenylsilicon dichloride, instead of yielding a derivative of silicoethylene, is transformed into closed- and open-chain compounds $(SiPh_2)_n$ in which *n* is not less than 4 (Kipping and Sands, *ibid.*, p. 830).

In an attempt to obtain some silicoethane derivatives from which silicoglycols might be prepared, the action of sodium on diphenylphenoxysilicon chloride was recently studied (Kipping, J., 1927, 2728); here again, instead of the desired product

$$OPh{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh,$$

octaphenylsilicotetrane and diphenyldiphenoxysilicane were formed, together with a small proportion of octaphenyldiphenoxysilicotetrane and other substances.

It was therefore of interest to study the action of sodium on various phenoxychlorosilicanes and for this purpose the mono-, di-, and tri-phenoxy-chlorides were prepared by treating silicon tetrachloride with phenol; they are all colourless liquids and are readily hydrolysed by water. When they are heated with excess of sodium in boiling xylene solution, they are all slowly attacked, giving a dark bluish-black deposit, and the whole of their chlorine is finally eliminated as sodium chloride. The filtered solution contains in all cases phenyl orthosilicate, $Si(OPh)_4$, the yield of which shows that practically all the phenoxy-groups in the original halogen compound are obtained in the form of the ortho-ester, as, for example,

$$2Si(OPh)_2Cl_2 + 4Na = Si(OPh)_4 + Si + 4NaCl.$$

Now the phenoxy-chloride when heated alone does not undergo any change, so the production of the ortho-ester is not due to interactions such as $2Si(OPh)_2Cl_2 = Si(OPh)_4 + SiCl_4$; it must be concluded, therefore, that the metal attacks some of the halogen compound, forming sodium phenoxide, which then reacts with the remainder to give the ortho-ester.

The insoluble product, freed from sodium and sodium chloride, is in all cases a grey powder, insoluble in all organic solvents. Different preparations from the different phenoxy-chlorides contain 38—40% of silicon; they give hydrogen with an aqueous solution of sodium hydroxide, and the same quantity also when warmed with water, but this quantity varies greatly with different samples from

a given phenoxy-chloride. These facts seem to show that the original insoluble material may consist largely of silicon, most of which is converted into silica or silicoformic acid by the action of water during its separation from the sodium and sodium chloride.

EXPERIMENTAL.

Interaction of Phenol and Silicon Tetrachloride.—Phenol ($2\frac{1}{4}$ mols.), dissolved in an approximately equal volume of benzene, is dropped slowly into boiling silicon tetrachloride (1 mol.). Hydrogen chloride is immediately evolved, but the reaction gradually slows down, and after all the phenol has been added the mixture is heated to, and kept at, 200° during 3 to 4 hours. The liquid is distilled (60 mm.) and the following products are collected: I, b. p. 170—195° (about 20%); II, b. p. 195—230° (35—40%); III, b. p. 230—265° (about 35%). The residue (2—5%) solidifies when cooled and consists principally of phenyl orthosilicate.

Phenoxytrichlorosilicane, $Si(OPh)Cl_3$, is isolated by systematically fractionating the crude product (I) through a 12″ rod and disc column. It is a somewhat viscous liquid of high density, b. p. 183—186°/60 mm.; it fumes strongly in moist air, is miscible with most anhydrous solvents, and is readily hydrolysed by water (Found in two different preparations: Cl, 46·6, 46·7. $C_6H_5OCl_3Si$ requires Cl, 46·8%).

Diphenoxydichlorosilicane, $Si(OPh)_2Cl_2$, is obtained by the further fractionation of the crude product (II) in a similar manner. It is a viscous fuming liquid, b. p. 215—218°/60 mm. and 199·5—202°/40 mm., similar in properties to the monophenoxy-derivative (Found in three different preparations: Cl, 24·6, 24·9, 25·0. $C_{12}H_{10}O_2Cl_2Si$ requires Cl, 24·9%).

Triphenoxychlorosilicane, $Si(OPh)_3Cl$, isolated from the fraction (III) in like manner, boils at 252—256°/60 mm. and at 235—239°/25 mm. It is very viscous, miscible with most anhydrous solvents, and fumes only slightly in moist air (Found in two different samples: Cl, 10·3, 10·2. $C_{18}H_{15}O_3ClSi$ requires Cl, 10·3%).

The solid residue from the first distillation crystallises from light petroleum in long colourless prisms, m. p. 48°. It was identified as phenyl orthosilicate by analysis and by its properties.

The above results seem to prove that the three phenoxy-chlorides do not interchange chlorine atoms and phenoxy-groups at the given temperatures; the compounds are also stable at higher temperatures. Samples of the mono- and of the di-chloro-derivative were heated almost to ebullition under atmospheric pressure during about 6 hours and then distilled under 60 mm.; the boiling points of the original samples had undergone no change.

Action of Sodium on Phenoxytrichlorosilicane.—Phenoxytrichlorosilicane (15 g.) is dissolved in pure xylene (3—4 vols.), sodium (5 g.) added, and heat applied. A reaction soon sets in and a bluish-black crust is formed on the metal. The flask is vigorously shaken at intervals and the heating is continued until, at the end of about 15 hours, a few drops of the filtered liquid treated with aqueous acetone give a neutral extract. Hydrogen chloride is evolved during the operation, but apparently the gas is free from any silicon compound.

The solution is filtered in a dry atmosphere, and the black residue washed with dry xylene two or three times; the combined filtrate and washings are then evaporated under reduced pressure. The product is a brown syrup, the weight of which (6·5 g.) corresponds almost exactly with that calculated for $4Si(OPh)Cl_3 + 12Na = Si(OPh)_4 + 12NaCl + 3Si$. When cooled, it solidifies almost completely, and after recrystallisation from light petroleum it melts at 47—48° and does not depress the melting point of phenyl orthosilicate. The oily mother-liquor from the crystalline ortho-ester gives a further crop of this compound when cooled in ice; the oil which then remains seems to be merely phenyl orthosilicate mixed with a very small proportion of some impurity; it is completely hydrolysed by aqueous alkali [Found: Si, 7·3. Calc. for $Si(OPh)_4$: Si, 7·0%].

The almost black residue (see above) is added in small portions at a time to a mixture of alcohol and excess of glacial acetic acid, and the whole is then poured into a large volume of water. The insoluble matter, which rises to the surface of the aqueous solution as a dark grey curdy precipitate, continually gives off bubbles of gas. It is separated, washed with water, alcohol, and ether successively, and dried over sulphuric acid under reduced pressure. The product, light grey in colour, does not lose in weight at 150°, and contains 38·5% of silicon. It is attacked by a solution of sodium hydroxide, but 1 g. gives only 50·1 c.c. of hydrogen at N.T.P.,* a fact which shows that it consists principally of silica. An equal volume of hydrogen is obtained when hot water is used instead of sodium hydroxide solution.

The Action of Sodium on Diphenoxydichlorosilicane.—The diphenoxy-derivative (35·9 g.) is heated with excess of sodium in exactly the same way as the monophenoxy-compound; the products are isolated as already described. The weight of the crude soluble matter is 20 g., which agrees with that calculated for $2Si(OPh)_2Cl_2 + 4Na = Si(OPh)_4 + 4NaCl + Si$, and this product, which crystallises

* The volume of hydrogen given by 1 g. of silicon, silicoformic acid, and silico-oxalic acid would be 1596, 338, and 162 c.c., respectively.

when cooled, is practically pure phenyl orthosilicate. The insoluble residue contained 38·1% of silicon, and 1 g. gave 139 c.c. of hydrogen with sodium hydroxide solution and 146 c.c. with hot water, so that the proportion of silicon or other hydrogen-giving substance in this preparation was much larger than in the previous insoluble product.

A totally different sample gave Si = 38% and 1 g. gave 89·1 c.c. of hydrogen. A third sample, in the isolation of which care had been taken to keep the alcohol–acid mixture very cold and the contact of the product with water as short as possible, gave a hydrogen value of 209·3; another portion of the same preparation, during the isolation of which the acid–alcohol mixture was allowed to get hot, but which had been kept in contact with water during the same length of time as the first portion, gave a hydrogen value of 177 and contained 37·8% of silicon. The fact that the hydrogen values of different samples containing practically the same percentage of silicon vary from 50·1 c.c. to 209 c.c. seems to show that the hydrogen-giving compound is mainly silicoformic acid.

Two different samples of the insoluble matter were submitted to combustion [Found: (sample I) C, 7·8, 7·7; H, 1·8, 1·8; (sample II) C, 7·7; H, 1·7%]. When heated with alkali, these samples gave quantities of sodium phenoxide corresponding with about one-quarter of the carbon present; this phenoxide was possibly formed from occluded phenyl orthosilicate. The alkaline solutions gave with acids gelatinous precipitates which, when thoroughly washed and dried, charred when warmed with concentrated sulphuric acid and contained 30·6—30·8% of silicon. As the organic matter in these precipitates seems to consist of phenyl groups directly combined with silicon, it may be surmised that the original grey insoluble matter contains some complex condensation product of phenylsilicoanic acid and silicic acid.

The Action of Sodium on Triphenoxychlorosilicane.—The procedure was identical with that described in previous cases; 21 g. of the compound gave after 12 hours 16·6 g. of crude phenyl orthosilicate and 0·6 g. of a grey insoluble residue, which contained 39·1% of silicon and had a hydrogen value of 120.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 20th, 1929.*]

CLVII.—*Organic Derivatives of Silicon. Part XL. Attempts to prepare Unsaturated Compounds from Phenylsilicon Trichloride.*

By Frederic Stanley Kipping, Arthur George Murray, and (in part) John Gwilliam Maltby.

At the present time there is no evidence of the existence of a compound containing the group $>Si{=}C<$ (Kipping, J., 1927, 104), and when dichlorides R_2SiCl_2 are heated with sodium the products do not contain the complex $>Si{=}Si<$ but are either open- or closed-chain structures consisting entirely of $-SiR_2-SiR_2-$ groups (Kipping and Sands, J., 1921, **119**, 830, 848; Kipping, J., 1923, **123**, 2590: 1924, **125**, 2291; 1927, 2719); the only known case of unsaturation in silicohydrocarbons, as judged by the property of combining with iodine, is that of octaphenylsilicotetrane, which contains 2 atoms of tervalent silicon.

Several attempts have been made during the last ten years to produce unsaturated silicon compounds by the action of sodium on phenylsilicon trichloride under different conditions. The results seem to have shown that $SiPh{\equiv}SiPh$ cannot be obtained in this way; in its place there results a mixture of very complex products, most of which apparently are saturated compounds.

At about 180°, in the absence of a solvent, the trichloride is very slowly but almost entirely transformed into a greyish insoluble powder which contains 25·1—26·8% Si (SiPh requires 26·8%), does not combine with iodine or even with bromine and is not attacked by a mixture of piperidine and aqueous alkalis.

In boiling benzene or toluene solution, the action of sodium on the trichloride is inappreciable; experiments were therefore made with naphthalene as a solvent. At the boiling point of the solution, the reaction with sodium is definitely exothermic and is completed very much more rapidly than when no solvent is used, although the temperature is about the same in the two cases. Only a very small proportion of the product is insoluble in organic solvents; this contains a much larger percentage of silicon than the insoluble powder referred to above and, unlike the latter, gives hydrogen readily with caustic alkalis. The main product, fractionated from various solvents, gives preparations all of which contain oxygen; while some appear to contain $>SiPh_2$ groups, and possibly naphthyl radicals.

In benzene solution at about 150°, in a sealed tube, or in boiling xylene, the trichloride is attacked by sodium fairly readily at first, but prolonged heating is required to complete the interaction;

potassium was therefore added towards the end of the operation in most of the experiments with xylene. With either solvent there is only a small proportion of insoluble product, which seems to be similar to that obtained in naphthalene solution.

The soluble matter from the xylene solutions, prepared in an atmosphere of nitrogen, has been studied more closely than that obtained with other solvents. It is a pale yellow resin which, judging from its iodine absorption, contains only a small proportion of unsaturated, probably tervalent, silicon atoms. It is easily separated into two main fractions with cold acetone, and further fractionation gives a graded series of colourless powders together with preparations of a more gelatinous character.

All the fractions seem to be complex mixtures which either char without melting or liquefy over a wide range of temperature. The more soluble ones contain $>SiPh_2$ groups, a fact which shows that phenyl groups have been transferred from one silicon atom to another, just as are benzyl radicals during the interaction of sodium and dibenzylsilicon dichloride (Steele and Kipping, J., 1928, 1431); as in the latter case and also in that of diphenylsilicon dichloride, the trichloride gives with sodium metallic derivatives which impart a deep red colour to the xylene solution: if sodium phenyl is thus produced, it would no doubt react with $>SiPhCl$ to form $>SiPh_2$ groups.

Analyses of the freshly prepared, unfractionated, soluble material indicate the presence of at least 4% of oxygen; a further quantity of oxygen is absorbed at 120°, the material becoming much less soluble, but its glue-like character at that temperature prevents very accurate determinations; it does not seem to oxidise in the air at the ordinary temperature, although perhaps it may do so slowly in solution. The source of the oxygen present in the unexposed products has not been ascertained. When the reddish xylene solution is filtered, the filtrate sometimes effervesces distinctly; it rapidly becomes pale yellow on exposure to the air and gives an alkaline solution with water. If, therefore, some of the sodium in the solution is combined with silicon, a portion of the combined oxygen in those products which have been in contact with water may be due to the action of alkali on $>SiPhH$ groups. In order to make sure that the presence of oxygen was not the result of the hydrolysis of $>SiPhCl$ groups, the solution of the trichloride was always boiled with excess of metal until a portion of the filtered liquid gave with water an alkaline extract, and the product in the xylene solution, ignited with sodium, gave a negative halogen reaction. As some of the oxygen might be derived from sodium or potassium oxide, an experiment was made with sodium, which had

been melted in nitrogen and filtered through glass wool; the xylene filtrate seemed to be rather richer than usual in sodium derivatives but otherwise the product differed little, if at all, from previous preparations and contained about 4% of oxygen.

The results of many analyses seem to show that the more sparingly soluble fractions are composed principally of compounds containing oxidised $\geqslant$SiPh groups, whereas the components of the more soluble fractions contain in addition a considerable proportion of $>SiPh_2$ groups.

Cryoscopic determinations in benzene and in camphor show that the average molecular weight of the components of the most sparingly soluble fraction is about 5,000, that of the substances in the most soluble material being about 900. The crude product, therefore, seems to be a mixture of compounds containing from about 6 to at least 50 silicon atoms in their molecules.

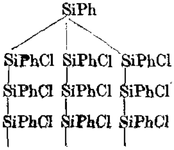
All the fractions are attacked by aqueous piperidine, and by aqueous alkalis in the presence of an organic solvent, with evolution of hydrogen and fission of Si–Si linkages. It was expected, therefore, that the principal product of fission would be orthophenylsiliconic acid, $SiPh(OH)_3$; that $>SiPh_2$ groups, if present, would give diphenylsilicanediol, $SiPh_2(OH)_2$; and that any silicon atoms not combined with carbon would yield orthosilicic acid. Further, if the preparations contained any compounds which were not attacked, or which gave crystalline fragments immune from further change, the investigation of such material might yield important information. Unfortunately, however, the identification of the products of fission is surrounded by difficulties; the organic hydroxides just formulated undergo a reversible condensation in the presence of alkalis and some of their numerous condensation products are not only insoluble in organic solvents (Kipping and Murray, this vol., p. 360) but are also very difficult to hydrolyse. Consequently it is not easy to ascertain in any given case whether or not all the Si–Si links have undergone fission; the material which does not become soluble in aqueous alkalis may be either an unchanged substance, a fragment, some stable condensation product, or a mixture of all these, and its ill-defined properties render its identification almost impossible.

When the more sparingly soluble preparations were heated with piperidine and alkali hydroxide until hydrogen ceased to be evolved, only a small proportion became soluble in aqueous alkalis; the solution gave with acids a gelatinous precipitate, which appeared to be a mixed condensation product of orthophenylsiliconic acid and orthosilicic acid. The material insoluble in aqueous alkali seemed to be a mixture of condensation products of orthophenyl-

siliconic acid and diphenylsilicanediol. The presence of the last-named compound in the products of hydrolysis of the most readily soluble preparations was definitely established. The hydrogen values of some samples of the original product and of many of the fractions were determined, but as the proportion of unchanged material, if any, could not be ascertained, and the presence of oxygen created other complications, the quantitative results afforded little information.

It will be evident from the above account that, under all the different experimental conditions, the trichloride is converted into a complex mixture of products, the components of which contain not only $\geqslant$SiPh and $>SiPh_2$ groups but also silicon atoms uncombined with carbon; some of the silicon atoms seem to be unsaturated, probably tervalent, but most of them have become saturated by combination with oxygen.

It may be suggested that in the first stages of the reaction silicon atoms are linked to give structures such as



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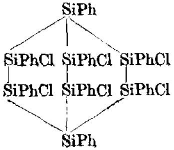


which increase in complexity so long as there is any unchanged trichloride present, until molecules containing fifty or more silicon atoms have been formed. As the supply of trichloride becomes exhausted, the further elimination of halogen probably leads to the production of bridged rings of different types. When this stage has been passed and, owing to steric influences, ring formation is brought to an end, the removal of the rest of the chlorine probably gives rise to tervalent silicon atoms; some of the halogen may also be displaced by sodium, and some by oxygen probably derived from sodium oxide. In addition some of the phenyl radicals are displaced by sodium with the probable formation of sodium phenyl, which then reacts with >SiPhCl groups; it is possible that some chlorine atoms are displaced by hydrogen present in the sodium.

In the course of the above work it was found that various silicon compounds such as "phenylsiliconic anhydride" and diphenylsilicanediol are completely converted into volatile products by evaporation with an aqueous solution of hydrogen fluoride.

EXPERIMENTAL.

Phenylsilicon Trichloride.—Phenylsilicon trichloride prepared in the ordinary way (J., 1912, **101**, 2113; 1914, **105**, 681) is not easily obtained in the pure state; fractions collected from about 148—153°/200 mm., after repeated distillation, contain some ethoxy-compound, probably $SiPhCl_2(OEt)$ (compare Kipping and Murray, J., 1927, 2734), and give alcohol on hydrolysis. When prepared by the modified method (*loc. cit.*) with the proportion $2SiCl_4 : 1\frac{1}{2}MgPhBr$. the pure trichloride (b. p. 152—153°/200 mm.) is easily isolated. The yield is about 100 g. from 170 g. of the tetrachloride (Found: Cl, 50·2, 50·5. $C_6H_5Cl_3Si$ requires Cl, 50·3%). The pure trichloride was used in all the xylene experiments; in the earlier ones the liquid which had been fractionated carefully and boiled at 198—200°/760 mm. was assumed to be pure.

Action of Sodium on the Trichloride.—(1) *No solvent.* The trichloride (10 g.) and sodium (4 g.) are heated in a flask with a 30″ air-condenser and a calcium chloride tube and when the metal has melted the flask is vigorously shaken; the temperature is then slowly raised to about 190°. The globules of sodium gradually become covered with a very dark brown crust, and after the lapse of some 8 hours, during which the flask is again shaken from time to time, decomposition seems to be complete. The dark granular mass is cooled, extracted with boiling benzene, and cautiously added to a mixture of alcohol and excess of glacial acetic acid; the solution is diluted with water, warmed, and filtered and the residue, a light brown powder, is thoroughly washed with water, alcohol, and benzene successively, and dried at 110°. The yield is about 4·6 g. (theoretical for SiPh, 5·4 g.).

Five different preparations gave Si = 26·5, 25·7, 26·8, 25·1, 26·3. Although these figures point to the formula SiPh (which requires Si, 26·8%), the later results seem to show that this product is a mixture and contains a considerable proportion of oxygen.*

(2) *Naphthalene as solvent.* The trichloride (10 g.), sodium (4 g.), and naphthalene (20 g.) are heated together in a flask fitted up as described and when the solids have melted the flask is vigorously shaken and again heated. Directly the mixture begins to boil, an exothermic reaction sets in and ebullition continues for some

* These experiments and also those with naphthalene were carried out by Mr. Maltby; later, the trichloride was heated with sodium in an atmosphere of nitrogen, but even after prolonged heating (20 hours) with a large excess of the metal, silicon halides were still present, a part of the product was soluble in benzene, and the insoluble portion gave hydrogen with alkali. These different results are no doubt due to the presence of atmospheric oxygen in the one case and not in the other.—F. S. K.

time without external heat; the metal becomes coated with a very dark brown spongy solid and the liquid turns yellow. When ebullition slackens, the contents of the flask are again boiled and vigorously shaken; at the end of about 15 minutes the solution is free from silicon halides.

The cooled product is mixed with benzene (250 c.c.), the solution filtered (with difficulty), and the residue well washed with boiling benzene, after which it is treated exactly as previously described. The insoluble product is a buff-coloured, amorphous powder (only about 0·25 g.). Five different samples gave Si = 33·9—34·7 (SiPh requires Si, 26·8%). It yields hydrogen very readily with caustic soda: three different samples gave, respectively, 1·0, 1·2, and 1·0 atoms of hydrogen per atom of silicon (SiPh should give 3 atoms), but about 25% was undissolved in each case; even if the undissolved matter yields no hydrogen, the results indicate that the rest of the material contains a very considerable proportion of oxygen. About 80% of the powder volatilised on evaporation with hydrofluoric acid; the residue contained only 15% of silicon. From these data it may be inferred that the insoluble product is a mixture of very complex compounds containing $\geqq$SiPh and $>SiPh_2$ groups as well as silicon atoms which are not combined with carbon; the residue after treatment with hydrofluoric acid seems to consist of derivatives of $>SiPh_2$ ($SiPh_2O$ requires Si, 14·2%).

The yellow benzene filtrate, which shows a green fluorescence, is submitted to steam distillation and the glue-like residue is dissolved in benzene and reprecipitated with alcohol; when dried, it is an amorphous yellow powder (about 5 g.). When this product is treated with cold acetone a portion dissolves readily, but the rest is only very sparingly soluble. The former is readily soluble in ether and carbon tetrachloride but practically insoluble in alcohol and glacial acetic acid; six different samples dried at 100° gave Si = 20—20·7% and when treated with sodium hydroxide evolved 0·95—1·06 atoms of hydrogen per atom of silicon (*M*, cryoscopic in benzene, 2100, 2200). The less soluble fraction is also practically insoluble in ether and alcohol but readily soluble in benzene and carbon tetrachloride; dried at 100°, it gave on the average Si = 24·5% and approximately one atom of hydrogen per silicon atom (*M*, cryoscopic in benzene, 4000). The proportions of these two fractions varied in different experiments from 3 : 2 to 2 : 3; with caustic alkalis, all the samples gave a considerable proportion of insoluble matter and the alkali solutions afforded gelatinous precipitates when acidified.

A large quantity of the crude benzene-soluble product was fractionally precipitated systematically from carbon tetrachloride

with ether and then from benzene with alcohol; the product was thus separated into eight fractions all consisting of yellow amorphous powders, which were dried at 100° and analysed with the following percentage results :—

Fraction.	C, %.	H, %.	Si, %.	O, %.	H (c.c.) per g.	Atoms of H per atom of Si.	
1	61·6	4·4	22·9	11·1	147	1·6	Practically insoluble in acetone.
2	62·4	4·0	21·9	11·7	132	1·5	
3	64·2	4·1	21·8	9·9	146	1·7	
4	—	—	—	—	—	—	Intermediate fractions.
5	66·8	4·0	—	—	—	—	
6	66·5	4·3	21·8	7·4	146	1·7	Readily soluble in acetone.
7	65·0	4·9	20·1	10·0	—	—	
8	—	—	—	—	—	—	Not examined.

These data show that the fractions 5, 6, and 7 contain a larger proportion of carbon than that required for Si : 6C. The proportion of hydrogen to carbon is much lower than that required for 5H : 6C, an indication that the material contains naphthyl radicals as well as $>SiPh_2$ groups. The large proportion of oxygen in these products is noteworthy, but as no particular precautions were taken to exclude air, its presence may be attributed, principally at any rate, to atmospheric oxidation.

(3) *Benzene as solvent.* The trichloride (10 g.) was heated with benzene and excess of sodium in sealed tubes at about 130° and while just below that temperature the tubes were shaken vigorously from time to time. After about 8 hours the temperature was raised to 150—160°; if then, at the end of 1—2 hours more, the globules of metal remained bright the heating was discontinued, and when cold, the deep reddish-yellow solution was quickly filtered. The residue, after being well washed with benzene and then treated as described above, afforded a grey powder (about 0·3 g.) insoluble in all organic solvents; different samples contained Si = 30—31·5% and gave about 1·35 atoms of hydrogen per atom of silicon with sodium hydroxide solution. When evaporated with hydrofluoric acid, about 45% of the powder volatilised, and the residue contained 13·5% of silicon. This material therefore seems to be very similar to the insoluble product from the experiments with naphthalene.

The benzene solution on evaporation afforded a pale yellow resin which contained C = 65·5, H = 4·7, Si = 22·6% (two concordant analyses) and gave about two atoms of hydrogen per silicon atom when heated with piperidine and sodium hydroxide solution. The carbon to silicon ratio is again greater than 6C : Si and although the product had been kept out of contact with air so far as possible during its isolation the analyses indicated the presence of about 7% of oxygen. The soluble product was systematically precipitated with alcohol from several different solvents; it gave a

graded series of preparations some of which were powders, sparingly soluble in acetone; others were glue-like in character and very readily soluble. The results of the further investigation of this material were very similar to those obtained with the product of the xylene experiments (see below) so that their description may be omitted.

(4) *Xylene as solvent.* The pure trichloride (50 g.) in pure xylene (500 c.c.) is heated with excess of sodium (approximately 25 g.) in an atmosphere of pure nitrogen. The reaction starts as soon as the solution begins to boil, the sodium becoming coated with a very dark brown or black deposit, which is detached by shaking the vessel vigorously from time to time. At the end of 10—12 hours the solution, as a rule, still contains silicon halide, to decompose which potassium (1 to 2 g.) was added in most of the experiments and the heating continued; after 5—7 hours longer, the solution acquires a deep brownish-red colour and a portion, if treated with water, gives an alkaline extract. The liquid is then filtered and the residue washed with hot xylene, both operations being conducted in an atmosphere of pure nitrogen; the washings are kept separate from the original filtrate.

The saline mass (which may immediately inflame on exposure to the air if much potassium has been used) is treated in the usual manner and the insoluble matter is washed with water, alcohol, and boiling benzene successively. The residue (about 2·5 g.) is a grey powder insoluble in all organic solvents; different samples contain Si = 30·8—32·3% and give hydrogen with sodium hydroxide solution; when evaporated with hydrofluoric acid six times, 80% volatilised and the glue-like residue contained only about 13% of silicon ($SiPh_2O$ requires Si, 14·2%), a fact which indicates the presence of $>SiPh_2$ groups in the powders; it seems, therefore, that this insoluble material is very similar to that obtained in the experiments with naphthalene and benzene.

Xylene filtrate. Three entirely different preparations, P_1, P_2, P_3, were examined; in the case of P_3 potassium was not used in the reaction (p. 1191). Aqueous extracts of portions of the solutions gave an alkaline reaction but only an inappreciable precipitate with silver nitrate; the products in the xylene solutions gave only traces of sodium chloride when they were ignited with sodium. The red filtrates became yellow if exposed to the air or if neutralised with glacial acetic acid or phthalic acid.

Absorption of oxygen and of iodine. A portion of the red xylene solution P_1 was treated with phthalic acid, the pale yellow liquid evaporated under reduced pressure, and the residue heated at 120° in an atmosphere of carbon dioxide during some hours. The sample

(1·18 g.) thus obtained was then exposed to oxygen in a flask connected with a manometer; no absorption occurred at the ordinary temperature after the expiration of several hours. At 100°, 27 c.c. were absorbed in 1 hour and an additional 10·6 c.c. in 2 hours more; the calculated increase in weight for 37·6 c.c. is 0·0536 g. and the observed increase was 0·0542 g., so that apparently there was no loss during oxidation and about 5% of oxygen was taken up. Further oxidation occurred at 160° and the product was then practically insoluble in benzene and chloroform.

A different preparation (about 1 g.) obtained by the direct evaporation of the red xylene solution P_2 absorbed only 18·3 c.c. of oxygen at 100—120° in the course of 10 hours and did not become insoluble in chloroform; this smaller absorption was possibly due to the more viscous character of the sample, as further oxidation occurred when fresh surfaces were exposed by treatment with solvents.

Another portion of P_1 was treated with iodine in benzene solution; only about one-ninth of its weight of iodine was absorbed, so that many more silicon atoms combined with oxygen than with the halogen. P_2 absorbed about one-quarter of its weight of iodine (after deducting the quantity which had combined with the sodium present), and P_3 (p. 1191) absorbed about one-tenth of its weight.

As there seemed to be no atmospheric oxidation at the ordinary temperature, the main bulk of P_1 was treated with a little warm acetone, containing sufficient acetic acid to decompose the sodium derivatives, and with warm benzene, in which it dissolved completely except for a little sodium acetate; the solution was then fractionally precipitated with acetone, these operations being repeated systematically until every fraction except the most soluble had been precipitated seven times. The fractions I (2 g.), II (3 g.), III (2 g.), and IV (3 g.) (I was the least soluble) were colourless powders, which charred without melting and dissolved freely in benzene and chloroform but were practically insoluble in acetone and ether; the most soluble fraction (VII, 3·5 g.) was rather gluelike in consistency, melted gradually from about 110° to 130°, and dissolved freely in warm acetone; fractions V (0·5 g.) and VI (1 g.) had intermediate properties and were not further examined.

Fraction I, ignited with sodium, yielded only traces of sodium chloride; when freed from solvent in a vacuum, it gave Si = 23·1% and 1·7 atoms of hydrogen per silicon atom. It was very difficult to burn; when mixed with copper oxide it gave C = 64·8, H = 4·8% as the average of three fairly concordant results. It was too sparingly soluble in camphor to give a measurable depression of the melting point, but a cryoscopic determination in benzene gave M = 5780.

Fractions III and IV (1·7 atoms of hydrogen per silicon atom), which seemed to be very similar to I in outward properties, were mixed together and precipitated with acetone from their solution in chloroform. After several operations, in which a small proportion of the most soluble material was discarded, the remainder, freed from solvent in a vacuum, was divided into two parts, one of which (A) was kept under reduced pressure and the other (B) was heated at 120° in air; the former lost in weight to a slight extent, but the latter gained about 4% in 3—4 days and was then practically insoluble in chloroform [Found for A: Si, 23·1; C, 64·1; H, 4·9; O (by diff.), 7·9%; 1·8 atoms of hydrogen per silicon atom. Found for B: Si, 22·1; C, 60·0; H, 4·4; O (by diff.), 13·5%; 1·1 atoms of hydrogen per silicon atom].

These results show that the fractions I—IV, which formed about two-thirds of the total product, are practically identical in composition and that the components of this material absorb nearly as much oxygen at about 120° as is already present.

The most soluble fraction (VII), precipitated from its acetone solution with alcohol and freed from solvent under reduced pressure, gave Si = 21·1, C = 69·3, H = 5·3, O = 4·3% and 2·1 atoms of hydrogen per atom of silicon; *M*, in camphor, 1132; *M*, cryoscopic in benzene, 934. It did not increase in weight appreciably when heated at 120° in the air during 3—4 days and was still completely soluble in warm acetone, but its hydrogen value decreased nearly 50%.

Fission products. Some of the more sparingly soluble material (II) was heated with a mixture of piperidine and a 20% aqueous solution of potassium hydroxide, in which it dissolved completely, until the evolution of hydrogen had ceased, and the aqueous layer was then separated so far as possible from the piperidine. The former, with excess of concentrated hydrochloric acid, gave a flocculent precipitate soluble in potassium hydroxide solution but insoluble in organic solvents; dried at 120°, it contained 24·1% o silicon. This result indicated a mixed condensation product o phenylsiliconic acid and silicic acid, since $(PhSiO)_2O$ contain Si = 21·9%. As, however, it might be a mere mixture of silic and phenylsiliconic acid, attempts were made to eliminate th former by evaporation with hydrofluoric acid, but only about 0·1% of residue was obtained. Experiments with phenylsilicon anhydride, prepared directly from the trichloride (Meads ar Kipping, J., 1914, **105**, 679), then showed that this compound decomposed by hydrofluoric acid, about 90% of it volatilising duri one treatment.

The separated piperidine solution, treated with excess of hydr

chloric acid, gave a glue-like material readily soluble in warm acetone but insoluble in a 20% aqueous solution of potassium hydroxide, by which it was only very slowly and incompletely hydrolysed. When dried, it contained 17·6% of silicon, and was apparently a mixed condensation product of phenylsiliconic acid and diphenylsilicanediol ($SiPh_2O$ requires Si, 14·2%). Subsidiary experiments showed that it would be useless to try to obtain the diol from this product by evaporation with hydrofluoric acid, since, like phenylsiliconic anhydride, the diol is completely decomposed if so treated.

In an attempt to isolate the diol a portion of fraction VII, which, judging from the analyses, contained a considerable proportion of $>SiPh_2$ groups, was boiled with alcoholic potash until hydrogen ceased to be evolved and the whole of the material had dissolved; the alcohol was then evaporated, and the filtered aqueous solution poured into a considerable excess of dilute acetic acid. In the course of about one minute crystals separated and, after filtration, the solution very slowly deposited glue-like matter. The crystalline product was identified as diphenylsilicanediol.

So far the experimental results explained why the ratio of carbon to silicon in part of the product is greater than 6C : Si, but the source of the oxygen in the fractionated material was still unknown. The red xylene solution P_2 was transferred to a flask filled with nitrogen, and the solution evaporated under reduced pressure; a little chloroform was then added without any air being admitted and by rapid evaporation the resin was frothed up into a bulky porous mass, which was heated at 100° in the same vessel during some hours under low pressure to free it from solvents. This product gave Si = 18·0% (after correction for the sodium salts present) and 1·5 atoms of hydrogen per silicon atom. Since $\geqslant$SiPh gives 3 and $>SiPh_2$ gives 2 atoms of hydrogen for each atom of silicon, it is obvious that this product already contains oxygen or else a considerable proportion of it is not decomposed by alkali. The rest of the xylene solution P_2 was treated with a few drops of glacial acetic acid without admission of air; a crystalline precipitate of alkali acetates was produced and the pale yellow solution was then evaporated and the residue extracted with pure ether; the filtered extract, concentrated and then frothed up, gave a brittle resin. The portion not dissolved by ether was treated with chloroform, and the solution filtered from the residue of alkali acetates (about 0·3 g.); the filtrate was evaporated and frothed up. In all these operations air was excluded so far as possible.

When freed from solvent under reduced pressure in an inert atmosphere, the product (2·5 g.) from the ethereal solution gave Si,

18·3; C, 70·8; H, 5·7%; 1·6 atoms of hydrogen per silicon atom, and the product (0·5 g.) from the chloroform solution gave Si, 20·1%; 1·5 atoms of hydrogen per silicon atom.

It will be seen from these results that, in spite of the precautions taken, the product in P_2 had combined with oxygen in the course of its preparation or subsequent treatment.

The red xylene solution P_3 had been prepared without using any potassium, because the ordinary balls of this metal might well contain appreciable quantities of oxide. The sodium which was used was melted and then filtered through glass wool in an atmosphere of nitrogen into the nitrogen-filled reaction flask containing the xylene solution of the trichloride (13 g.). The heating was continued during about 15 hours; the solution then gave as usual an alkaline reaction with water, and a portion of the resin obtained by evaporating the xylene gave only a faint indication of halogen when it was ignited with sodium. The whole of the red solution (filtered in nitrogen) was treated with a few drops of glacial acetic acid, filtered from a bulky precipitate of sodium acetate, and evaporated under reduced pressure, air being excluded in these operations so far as possible. The residue contained (two concordant analyses) Si = 20·3, C = 69·4, H = 5·5, O (by diff.), 4·8%, and it gave 2·1 atoms of hydrogen per atom of silicon. Heated in the air at 120° during many hours, it became only partly soluble in benzene and then gave only 0·9 atom of hydrogen per atom of silicon.

Part of the material used in this investigation was purchased with the aid of a grant from the Government Grant Committee of the Royal Society. The authors wish to acknowledge their gratitude for this help.

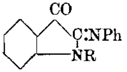
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 20th, 1929.*]

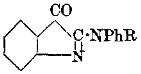
CLVIII.—*Isatin Anils. Part I. The Isomerism of Isatin-2-anil.*

By ROBERT KENNETH CALLOW and EDWARD HOPE.

THE existence of two tautomeric forms of isatin-2-anil (I and II; R = H) was discovered by Pummerer (*Ber.*, 1911, **44**, 338, 810). The form to which the constitution (I) was assigned, the anil, separated from alcohol in yellowish-brown leaflets, and the anilide (II) formed violet prisms from benzene. Both forms melted at 126°. Confirmation of this isomerism was afforded by the synthesis of the

isomeric methyl derivatives. In the course of an investigation of the acylation of isatin anils we have been able to obtain additional

(I.) 

 (II.)

(III.) $C_6H_4<\begin{matrix}CO\cdot CO\cdot NHPh\\ NHBz\end{matrix}$

$C_6H_4<\begin{matrix}C<\begin{matrix}NPh\\ CO\cdot NHPh\end{matrix}\\ NHBz\end{matrix}$ (IV.)

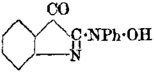
proof of Pummerer's conclusions by preparing directly from isatin-2-anil the isomeric benzoyl derivatives corresponding to the tautomeric forms (I) and (II). N-*Benzoylisatin*-2-*anil* (I; R = Bz) is readily prepared by heating isatin-2-anil with benzoic anhydride. Its constitution is established by its hydrolysis to *o*-benzamidophenylglyoxylic acid and aniline, and by its ready conversion in boiling alcoholic solution in the presence of a trace of hydrochloric acid into o-*benzamidophenylglyoxylanilide* (III) by opening of the pyrrole ring. The last compound was also obtained by the reaction of the chloride of the acid with aniline. An analogy to the opening of the pyrrole ring of *N*-benzoylisatin-2-anil was found in the transformation of *N*-benzoylisatin under similar conditions to *o*-benzamidophenylglyoxylic acid and its *ethyl* ester. Again, when *N*-benzoylisatin-2-anil was heated with aniline the product was o-*benzamidophenylglyoxylanilideanil* (IV), the water formed in the reaction having evidently brought about immediate opening of the ring.

The action of benzoyl chloride on isatin-2-anil in benzene or nitrobenzene solution at the ordinary temperature yielded *N*-benzoylisatin-2-anil and the hydrochloride of isatin-2-anil. In pyridine solution, however, *isatin*-2-*benzanilide* (II; R = Bz) was obtained. This compound was very readily decomposed by water with the formation of isatin and benzanilide, and its constitution is, therefore, quite clear.

While this work was in progress, the original assumption of Pummerer regarding the tautomerism of isatin-2-anil was called into question by Rupe and Apotheker (*Helv. Chim. Acta*, 1926, **9**, 1049). These authors obtained by reduction of the product of condensation of isatin and β-phenylhydroxylamine (Rupe and Stöcklin, *ibid.*, 1924, **7**, 557) a substance to which they assigned the constitution of the lactim form of isatin-2-anil (I; R = H). It was obviously different from either of the forms described by Pummerer, which, they concluded, were simply polymorphic forms of the lactam structure. The grounds on which their conclusions were based were, first, the assumption that β-phenylhydroxylamine

ndensed with isatin in the 2-position, and, secondly, the non-entity of the product with α-anilinoindoxyl (isatin*leuco*-2-anil) 'ummerer and Göttler, *Ber.*, 1910, **43**, 1376), although the elemen-ry analysis corresponded more closely with the latter substance. was found necessary to postulate peculiar mechanisms of reaction explain the formation of the 3-semicarbazone, 3-oxime, and phenylhydrazone from the new " isatin-2-anil " and of the 2-semi-ırbazone, 2-oxime, and 2-phenylhydrazone from the previously nown forms of isatin-2-anil.

Consideration of their arguments convinced us that the first ssumption of the constitution of " isatin-β-phenylhydroxylamine " as erroneous. It is certain that the reactive carbonyl group in atin is that in position 3, and it is *a priori* likely that β-phenyl-ydroxylamine will react with this. Furthermore, it is not per-issible (as Rupe and Stöcklin suppose) to assume that isatin chloride eacts preferentially with its halogen with reagents having the apacity of reacting with a carbonyl group, for we have found that satin chloride reacts with aniline to yield isatin-3-anil and isatin-lianil. If, then, this substance were not isatin-2-β-phenylhydroxyl-mine (V) but isatin-3-anil *N'*-oxide (VI), it would yield on reduction -anilino-oxindole (isatin*leuco*-3-anil) (VII), already prepared by Pummerer and Göttler (*loc. cit.*). We have now found, by direct omparison, that the product obtained by the method of Rupe and Apotheker is identical with 3-anilino-oxindole, and our suggestion or the actual course of the reaction is therefore confirmed.



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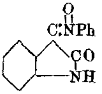
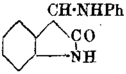


(VI.)



(VII.)

It would appear that the constitutions assigned to certain other derivatives prepared by Rupe and his collaborators should be revised in the light of these results (*locc. cit.* and *Helv. Chim. Acta*, 1927, **10**, 926). The true isatin-2-β-phenylhydroxylamine or 2-phenylimino-indoxyl *N'*-oxide appears to have been prepared by Alessandri (*Gazzetta*, 1927, **57**, 195) by condensation of *o*-nitrophenylacetylene with nitrosobenzene, and the by-product which we obtained in the condensation of indoxyl with nitrosobenzene (see experimental section) is probably identical with it.

In conclusion, we consider, on the basis of this correction of the results of Rupe and Apotheker, and of the additional evidence provided by the preparation of isomeric benzoyl derivatives, that there

is no need to modify the original hypothesis of tautomerism of isatin-2-anil put forward by Pummerer.

EXPERIMENTAL.

Isatin-2-anil.—Attempts made to prepare isatin-2-anil by the condensation of isatin chloride with aniline were unsuccessful, although it is stated by Borsche, Weussmann, and Fritzsche (*Ber.*, 1924, **57**, 1770) that 5-iodoisatin-2-anil is formed from 5-iodoisatin chloride in this way.

(*a*) Isatin chloride (2 g.) and aniline (1·1 g.; 1 mol.) in benzene were heated under reflux for 15 minutes. Isatin-3-anil was the only product which could be isolated.

(*b*) In an experiment in which double the amount of aniline was employed, isatindianil and a substance, m. p. 165—180°, insoluble in light petroleum, were separated. In neither (*a*) nor (*b*) could any trace of isatin-2-anil be recognised.

A small quantity of isatin-2-anil was prepared by the condensation of indoxyl with nitrosobenzene (Pummerer and Göttler, *Ber.*, 1909, **42**, 4269; Pummerer, *Ber.*, 1911, **44**, 338), but this method was rather troublesome. Examination of the red substance obtained as a by-product showed that it was not isatindianil, as suggested by Pummerer and Göttler, but had the composition $C_{14}H_{10}O_2N_2$ (Found: C, 70·8; H, 4·4; N, 11·9; *M*, by Rast's method, 255. Calc.: C, 70·6; H, 4·2; N, 11·8%; *M*, 238). The substance was moderately easily soluble in boiling alcohol, from which it separated in fine, scarlet, flat needles, m. p. 196—197° (corr., decomp.). The *m. p. was depressed by mixture with isatin-3-anil N′-oxide. Isatin* was obtained by decomposition with dilute hydrochloric acid. The decomposition with 10% sulphuric acid, as described by Alessandri (*loc. cit.*) in the case of 2-phenyliminoindoxyl *N′*-oxide [m. p. 195—196° (decomp.)], yielded only a solution which rapidly darkened in the air, and instead of *p*-aminophenol, only a dark material of high melting point could be isolated. The qualitative solubilities of the substance in various solvents agreed completely with those recorded by Alessandri. When the substance was boiled with aqueous permanganate solution, the odour of nitrosobenzene was perceptible. The amount of substance available did not permit further examination.

The most convenient method for the preparation of isatin-2-anil was found to be a modification of the process of Sandmeyer (*Z. Farben- und Textilchemie*, 1903, **2**, 129). The isatin-2-anil obtained by treatment of oxalic diphenylamidine thioamide with sulphuric acid was, however, always accompanied by isatin-3-anil, and it was found better to proceed directly from hydrocyanocarbodiphenyl-

iide * to isatin-2-anil by treatment with aluminium chloride as scribed in D.R.-P. 277396. The scarlet isatin-2-anil hydrochloride tained was separated from as much as possible of the water and enzene by filtration and churned with water, and a slight excess of dium carbonate added. The crude isatin-2-anil was dried on rous plate and crystallised from ether. Yield: 50—60% of the eoretical; m. p. 126° (corr.).

N-*Benzoylisatin-2-anil* (I; R = Bz).—(a) *Benzoylation with nzoic anhydride*. Isatin-2-anil (10 g.) and benzoic anhydride 7·5 g.; 2 mols.) were mixed and heated at 100° for 2 hours. The ixture was then poured into alcohol (250 c.c.). On scratching, e product separated as needles (9 g., m. p. 169—172°). Recrystalsed from 50 parts of boiling alcohol, N-*benzoylisatin-2-anil* was btained as fine, bright red, prismatic needles, m. p. 172·5—173° orr.) (Found: C, 77·2; H, 4·3; N, 8·5. $C_{21}H_{14}O_2N_2$ requires , 77·3; H, 4·3; N, 8·6%). It was moderately easily soluble in enzene, slightly soluble in ether, and practically insoluble in light etroleum.

The colour of the solution from which the crude *N*-benzoylisatin--anil separated changed from dark brown to light red on standing r warming. After removal of alcohol and benzoic ester the residue vas separated into isatin, benzoic acid, and benzanilide. In the ight of the results described below, it seems likely that isatin-2-enzanilide was formed in the reaction and subsequently decomposed.

(b) *Benzoylation with benzoyl chloride in benzene solution*. Dry satin-2-anil (4·5 g.) was dissolved in dry benzene (200 c.c.), benzoyl chloride (7 g., freed from hydrogen chloride by distillation under educed pressure) added, and the mixture kept for 2 days. A light red, crystalline precipitate was formed, which, when removed, washed, and dried, melted at 205° (decomp.) and was identified as isatin-2-anil hydrochloride. The solution was evaporated under reduced pressure, and the pasty residue washed with light petroleum. After two recrystallisations of the solid from benzene and light petroleum, nearly pure *N*-benzoylisatin-2-anil was obtained. The amounts of the hydrochloride (2·6 g.) and of *N*-benzoylisatin-2-anil (2·7 g.) separated were approximately equivalent. Another method of working-up adopted at first and involving treatment with water led to the separation only of isatin, benzanilide, and benzoic acid.

No indigoid substance was formed when *N*-benzoylisatin-2-anil

* The hydrocyanocarbodiphenylimide was always accompanied by a substance resembling it in appearance, but differing in solubility in alcohol. It melted at 186—187° (Found: C, 77·65; H, 5·19; N, 17·1%. $C_{21}H_{16}N_4$ requires C, 77·8; H, 4·9; N, 17·3%). This substance has not yet been examined in detail.

was treated with ammonium sulphide in alcoholic solution. The addition of caustic soda solution to the alcoholic solution gave a blue colour which disappeared on acidification. The ethereal extract of the blue solution was red. This reaction is also given by isatin-2-anil and *N*-methylisatin-2-anil, but not by isatin-3-anil. The addition of sodium hyposulphite to the alkaline solution caused the blue colour to disappear, probably because of the formation of the "leuco-anil," but it returned on shaking with air.

Hydrolysis of N-*Benzoylisatin-2-anil.*—*N*-Benzoylisatin-2-anil (1 g.) was boiled under reflux with concentrated hydrochloric acid (35 c.c.) for 10 minutes. After cooling, the pale yellow solid was collected and dried. It melted at 192—193·5°, and was identified as *o*-benzamidophenylglyoxylic acid (Schotten, *Ber.*, 1891, **24**, 774) by a mixed melting-point determination with an authentic specimen obtained as described below. Yield: 0·6 g. (75% of the theoretical). Basification of the solution and extraction with ether yielded aniline.

o-*Benzamidophenylglyoxylanilide* (III).—*N*-Benzoylisatin-2-anil (0·5 g.) was boiled under reflux for 20 minutes with 50% aqueous alcohol (100 c.c.), to which one drop of concentrated hydrochloric acid had been added. The *N*-benzoylisatin-2-anil slowly dissolved and the colour of the solution changed to pale yellow. On cooling, pale yellow crystals (0·24 g.) separated. After two recrystallisations from 70% aqueous alcohol, very pale yellow, microscopic needles of o-*benzamidophenylglyoxylanilide*, m. p. 183—184° (corr.), were obtained (Found: C, 73·7; H, 4·8; N, 8·0. $C_{21}H_{16}O_3N_2$ requires C, 73·3; H, 4·6; N, 8·1%).

Treatment of the compound with concentrated hydrochloric acid yielded a material which did not melt below 330°. Hydrolysis by caustic alkali was, however, simpler. The compound (1 g.) was boiled under reflux with 2*N*-sodium hydroxide solution (25 c.c.) until complete solution took place (½ hour). Extraction of the cold solution with ether gave aniline, and from the remaining liquid, after acidification, isatin and benzoic acid were separated.

The constitution assigned to o-benzamidophenylglyoxylanilide was confirmed by synthesis, after two unsuccessful attempts. (1) Mixture of *o*-benzamidophenylglyoxylic acid and aniline in ether gave the *aniline* salt, m. p. 120—121° (corr., decomp.) (Found: N, 7·8. $C_{21}H_{18}O_4N_2$ requires N, 7·7%). After treatment of the aniline salt with phosphorus pentachloride in benzene, the acid alone was recovered. (2) When *o*-benzamidophenylglyoxylic acid was boiled with aniline and a crystal of iodine for a few minutes, and excess of aniline removed by dilute hydrochloric acid, a white precipitate of *o*-benzamidobenzaldehyde (Bischler and Lang, *Ber.*,

1895, **28**, 287) was obtained. It formed fine needles, m. p. 73—74°, from dilute acetic acid (Found: N, 6·0. Calc. for $C_{14}H_{11}O_2N$: N, 6·2%).

Finally the following method was successful. A large excess (20 c.c.) of thionyl chloride was shaken with *o*-benzamidophenylglyoxylic acid (2·5 g.), which dissolved with slight evolution of heat. The liquid was evaporated on the water-bath to 5 c.c., and the remainder of the thionyl chloride removed by two further evaporations to 5 c.c. after dilution with benzene. Attempts to isolate the chloride by adding smaller amounts of thionyl chloride to the acid suspended in benzene, or evaporation of the solution to dryness, yielded a dark, insoluble solid, m. p. 205—207°, which decomposed on keeping. The solution of the chloride was diluted with ether and added, drop by drop, to aniline (0·9 g.) dissolved in ether, in the presence of potassium carbonate. After addition of water, the emulsion was extracted with ether. The ethereal solution, washed with dilute acid and dried, yielded the impure anilide (1·6 g.) when evaporated. After recrystallisation, its identity with the product from *N*-benzoylisatin-2-anil was confirmed by a mixed melting-point determination.

N-Benzoylisatin.—Repetition of the preparation by the method of Heller (*Ber.*, 1903, **36**, 2764)—the action of benzoyl chloride upon isatin—led to the isolation of a product which, fractionally crystallised from dilute acetic acid, was separated into *N*-benzoylisatin, m. p. 213—214° (corr.), and an equal amount of *o*-benzamidophenylglyoxylic acid, which was more soluble.

N-Benzoylisatin was more easily prepared by heating isatin (12 g.) with benzoic anhydride (36 g.; 3 mols.) for 1 hour at 150—160°. After cooling, the solid product was ground with a little alcohol, and the insoluble residue of *N*-benzoylisatin (13·5 g.) purified by recrystallisation from glacial acetic acid.

Ring Scission of N-Benzoylisatin.—*N*-Benzoylisatin (6 g.), when boiled under reflux for 1 hour with 50% aqueous alcohol (400 c.c.) to which four drops of concentrated hydrochloric acid had been added, gradually dissolved, and, on evaporation to small bulk, oil and solid separated. The solid was dissolved by sodium carbonate solution, and the oil removed. Acidification of the solution precipitated *o*-benzamidophenylglyoxylic acid (3·2 g.). The oil (1·4 g.) solidified on standing, and on recrystallisation from dilute acetic acid gave *ethyl* o-*benzamidophenylglyoxylate* as colourless needles, m. p. 80° (corr.) (Found: N, 4·7. $C_{17}H_{15}O_4N$ requires N, 4·7%). The ester was rapidly hydrolysed to the acid when warmed with 2*N*-sodium hydroxide.

o-Benzamidophenylglyoxylic acid was conveniently prepared by

warming *N*-benzoylisatin (18·8 g.) for several minutes with dilute sodium hydroxide solution (2·6 g. in 170 c.c.). The solution was quickly cooled, filtered, and the acid precipitated by addition of hydrochloric acid. The precipitate was freed from isatin and benzoic acid by washing with hot water. Yield, 17·5 g. After repeated recrystallisation from dilute acetic acid, it had m. p. 196—197° (corr., decomp.) (Schotten, *loc. cit.*, gives 188°).

o-*Benzamidophenylglyoxylanilidoanil* (IV).—*N*-Benzoylisatin-2-anil (0·5 g.) was heated on the water-bath for a few minutes with aniline (2 c.c.) and a crystal of iodine. Yellow crystals separated when the mixture was poured into alcohol, and, after recrystallisation from 50 parts of benzene, o-*benzamidophenylglyoxylanilidoanil* was obtained as canary-yellow, microscopic needles, m. p. 204—205° (corr., decomp.) (Found: C, 77·6; H, 5·1; N, 10·0. $C_{27}H_{21}O_2N_3$ requires C, 77·3; H, 5·0; N, 10·0%).

Isatin-2-benzanilide (II; R = Bz).—Benzoyl chloride (7·2 g.) was added to isatin-2-anil (10 g.) dissolved in dry pyridine (18 c.c.). After 5 hours the mixture was poured into water (400 c.c.), and the precipitate collected and dried in a vacuum without delay. The yield was practically theoretical. The crude product was dissolved in 4 parts of boiling dry toluene, and twice the volume of dry light petroleum (b. p. 100—110°) added; *isatin-2-benzanilide* then crystallised in crimson prisms, m. p. 131° (corr.) (Found: C, 77·6, 77·0; H, 4·5, 4·3; N, 8·7, 8·3. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3; N, 8·6%). It was moderately easily soluble in boiling light petroleum (b. p. 100—110°) and readily soluble in benzene or toluene. It was essential to use carefully dried pyridine in the benzoylation and dried solvents for recrystallisation, otherwise mixtures of isatin and benzanilide were obtained. If the crystals were allowed to remain in the air, they acquired a superficial coating of colourless plates of benzanilide. When isatin-2-benzanilide (0·5 g.) was boiled under reflux for 1 hour with water (50 c.c.), it became tarry, and crystals of benzanilide (0·25 g.) were then deposited. Filtered hot and allowed to cool, the solution deposited isatin (0·16 g.). Decomposition into these products took place immediately in dilute hydrochloric acid and rapidly in aqueous alcohol.

Isatin-3-anil N′-*Oxide* (VI).—The condensation of isatin and β-phenylhydroxylamine in boiling alcohol, as described by Rupe and Stöcklin, gave isatin-3-anil *N*′-oxide in 60% of the theoretical yield. Recrystallised from alcohol, it formed scarlet, flat needles, m. p. 217·5—219° (corr., decomp.) (Rupe and Stöcklin give 216°).

3-*Anilino-oxindole* (VII).—(*a*) A solution of isatin-3-anil *N*′-oxide (10 g.) in a mixture of glacial acetic acid (150 c.c.) and water (15 c.c.)

was raised to boiling, and zinc dust (about 10 g.) added in small portions until the colour of the solution had faded to pale gold. The solution was then rapidly filtered into a vessel filled with coal-gas; hot, air-free water (100 c.c.) was added, and the mixture allowed to cool. The white solid which separated (4·7 g.) was twice recrystallised from alcohol. It was found to be most important to protect the product from oxidation during recrystallisation, otherwise the product, *presumably contaminated with the products of oxidation*, separated as a caseous mass which was difficult to filter rapidly and preserve from oxidation. 3-Anilino-oxindole separated as colourless plates, m. p. 192·5° (corr., decomp.) in an evacuated capillary tube (Rupe and Apotheker, *loc. cit.*, give m. p. 176° in an open tube) (Found: C, 75·1; H, 5·5. Calc. for $C_{14}H_{12}ON_2$: C, 75·0; H, 5·4%. Calc. for $C_{14}H_{10}ON_2$: C, 75·7; H, 4·5%).

(*b*) Isatin-3-anil, prepared as described by Knoevenagel (*J. pr. Chem.*, 1914, **89**, 46), was reduced by zinc dust in aqueous acetic acid in the same way as isatin-3-anil *N'*-oxide, the same precautions being employed against oxidation. 3-Anilino-oxindole separated in colourless plates from alcohol, indistinguishable under the microscope from the product of reduction of isatin-3-anil *N'*-oxide. The substance had m. p. 192° (corr., decomp.) in an evacuated capillary tube, and this was unchanged by mixture with the product from isatin-3-anil *N'*-oxide. The solubilities of both products in light petroleum, ether, chloroform, and acetone were as described by Pummerer and Göttler (*loc. cit.*).

One of us (R. K. C.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant during part of the time he was engaged in this work.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, April 12th, 1929.*]

CLIX.—*The Mobility of Symmetrical Triad Prototropic Systems. Part V. A New Triad System (Methyleneazomethine).*

By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE.

THE present position relating to the study of mobile hydrogen tautomerism (prototropy) may be summarised in the statement that the ionic theory, although not directly proved, rests on a comprehensive body of indirect evidence of which the more important features are the following:

(1) *Mobility and Ionisation.*—A parallel exists between the mobility of prototropic systems and those properties, such as the alkylation, stability of alkali-metal salts to hydrolysis, alcoholysis ammonolysis, etc., which measure the tendency to ionisation of the mobile hydrogen atom and the stability of the anion. The recognition of this principle (Part I, Ingold and Piggott, J., 1922, **121** 2381) led to the discovery (Part II, *idem*, J., 1923, **123**, 1469) that indene, which although a hydrocarbon is peculiar in yielding relatively stable metallic "salts," is tautomeric and highly mobile.

(2) *Mobility and Constitution.*—In symmetrical triad systems a parallel exists between mobility and the facility of ionisation to be expected from the nature of the terminal atom of the system, the character of the central atom being relatively unimportant. Thus (Part I, *loc. cit.*; Part IV, Ingold and Shoppee, this vol., p. 447 this paper) systems of the types $^{-}$NH·CR:N^{-} and $^{-}$NH·N:N^{-} are highly mobile and, despite the difference in the central atom, no marked differences of mobility have been observed between them corresponding systems of the types $^{-}CH_2$·CR:CH^{-} and $^{-}CH_2$·N:CH^{-} are relatively static, but, again, exhibit only minor differences amongst themselves. The expected order of ease of ionisation is HC<HN(<HO<HF).

(3) *External Promotion of Mobility.*—In a given triad system external facilitation of prototropy could theoretically occur either directly by the attraction of a catalyst for the potentially mobile proton, or indirectly by the addition to the molecule of a catalyst in such a way as to increase the electron-restraint at the seat of ionisation; but the direct mechanism would be expected to be much the more effective. Actually, the most powerful catalysts for the promotion of mobility in intrinsically slightly mobile systems are found to be anions of high co-ordinating power, that is, entities known to have peculiarly strong proton affinity (Ingold, Shoppee, and Thorpe, J., 1926, 1480; Part IV; and this paper).

(4) *Internal Promotion of Mobility.*—In a given triad system the facilitation of prototropy by constitutional influences should correspond with the electron-affinity ($-I$), and capacity for electron-attraction ($-T$), of the groups present, and also on the degree of directness of the path for the internal transmission of their effects to the seat of ionisation. This consequence of the ionisation theory has been shown to constitute a satisfactory description of the very considerable mass of data at present available (Ingold, Shoppee, and Thorpe, *loc. cit.*; Ingold and Rothstein, this vol., p. 8; Part IV; and this paper; compare *Ann. Reports*, 1927, 106; 1928, 118).

(5) *Analogy with Reversible Additions.*—A correlation has been demonstrated between prototropic change and a large class of

reversible addition reactions (aldol, etc.) for which there is strong independent evidence of a corresponding ionic mechanism (E. H. Ingold and others, J., 1923, **123**, 1717; 1924, **125**, 435, 1319; 1925, **127**, 469; 1926, 1868, 1894; *Chem. and Ind.*, 1923, **42**, 1246).

(6) *Analogy with Anionotropy.*—An analogy has been demonstrated between the conditions for mobility in prototropic and anionotropic systems; and for the latter a corresponding ionic mechanism has been completely proved (Burton and Ingold, J., 1928, 904; Burton, *ibid.*, p. 1650).

The experimental portion of this paper records the outcome of a simple application of the above principles to aid the discovery of a new triad prototropic system, which we propose to term the "methyleneazomethine" system $>CH\cdot N{:}C< \rightleftharpoons >C{:}N\cdot CH<$. By arguments along the lines indicated (1—4, above) we reasoned that such a system, if terminated at either end by aryl groups, should be mobile in the presence of ethoxide ions in alcohol, and that for moderate concentrations the interconversion of a pair of isomerides should proceed readily at temperatures somewhat above the ordinary temperature. Accordingly, we prepared the methoxyazomethines formulated below, and found that at 85° in 1·45*N*-alcoholic sodium ethoxide each isomeride underwent rapid conversion into an identical mixture of the composition shown. The proportions are in complete agreement with the consideration referred to under (4), above:

$$(21{\cdot}1\%)\ p\text{-}MeO\cdot C_6H_4\cdot CH_2\cdot N{:}CH\cdot C_6H_5 \rightleftharpoons p\text{-}MeO\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_5\ (78{\cdot}9\%)$$

The experimental record also contains evidence that the methyleneazomethine system terminated by only a single phenyl group exhibits mobility in the presence of alkali at a considerably higher temperature, although in this case the change appears to be substantially unidirectional:

$$C_6H_5\cdot CH_2\cdot N{:}CH_2 \longrightarrow C_6H_5\cdot CH{:}N\cdot CH_3$$

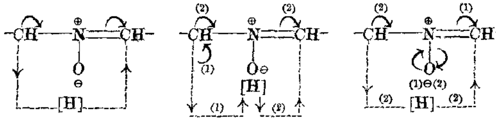
Direct demonstration, or strong presumptive evidence, of prototropic mobility was previously available for eleven out of the twelve formal triad systems constituted from the elements carbon, nitrogen, and oxygen. The outstanding case was the methyleneazomethine system, so the work now described completes a series.

Although prototropic mobility in the methyleneazomethine system has not, to our knowledge, previously been demonstrated, the statement that it has not previously been under observation would require the following qualification. Behrend (*Annalen*, 1891, **265**, 238), Neubauer (*ibid.*, 1897, **298**, 187), and Wegener (*ibid.*,

1900, 314, 231) have shown that isomeric substitution products of benzaldoxime *N*-benzyl ether undergo a reversible interconversion which may be represented thus:

$$R\cdot C_6H_4\cdot CH_2\cdot \overset{\oplus}{N}(\rightarrow O^{\ominus}){:}CH\cdot C_6H_5 \rightleftharpoons R\cdot C_6H_4\cdot CH{:}\overset{\oplus}{N}(\rightarrow O^{\ominus})\cdot CH_2\cdot C_6H_5$$

This may or may not be a methyleneazomethine triad change. The question at issue relates to the part played by the negative oxygen atom, and the possibilities are (A) that it takes no direct part, (B) that it receives and hands on the mobile proton, and (C) that, without accepting the proton, it hands on and then recovers its negative charge. In the first case the process represents simple methyleneazomethine prototropy; but in the second and third it does not, because in the former the proton-transfers, and in the latter the electron-transfers, are not those characteristic of the methyleneazomethine triad system. In short, the example is a complex one which it is impossible in the present state of knowledge definitely to assign to any recognised category.



(A.) (B.) [(1) precedes (2)] (C.)

Experimental.

p-*Methoxybenzylidenebenzylamine* was prepared by heating together *p*-anisaldehyde (1 mol.) and benzylamine (1 mol.) at 100° for 0·5 hour in an atmosphere of hydrogen. The product, dissolved in ether, was washed successively with 2% aqueous acetic acid and dilute sodium hydrogen carbonate solution, and dried with anhydrous sodium acetate; it then solidified after evaporation of the ether, and crystallised from ligroin in prisms, m. p. 42° (Found: C, 80·4; H, 6·6. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·6%).

When boiled for 0·5 hour with 2*N*-sulphuric acid, the base was completely hydrolysed, the aldehydic product being pure anisaldehyde and the basic product pure benzylamine. Therefore, no isomerisation of the azomethine occurs under the conditions stated. *Benzylamine picrate* separates from alcohol in needles, m. p. 198° (decomp.) (Found: C, 46·4; H, 3·6. $C_{13}H_{12}O_7N_4$ requires C, 46·4; H, 3·6%).

Benzylidene-p-*methoxybenzylamine*, similarly prepared from *p*

methoxybenzylamine and benzaldehyde, was a colourless oil, b. p. 217°/17 mm. (Found : C, 79·7 ; H, 6·6. $C_{15}H_{15}ON$ requires C, 80·0 ; H, 6·6%).

On hydrolysis under the conditions recorded above, it yielded pure benzaldehyde and pure *p*-methoxybenzylamine only. p-*Methoxybenzylamine picrate* separates from alcohol in prisms, m. p. 188° (decomp.) (Found : C, 46·0 ; H, 3·85. $C_{14}H_{14}O_8N_4$ requires C, 45·9 ; H, 3·85%), and the *benzoate* from chloroform–ligroin in needles, m. p. 135° (Found : C, 69·7 ; H, 6·5. $C_{15}H_{17}O_3N$ *requires* C, 69·5 ; H, 6·6%).

Interconversion. Either isomeride was heated for 2 hours at 85° with 30 parts of 1·45*N*-alcoholic sodium ethoxide, and the product isolated by pouring the mixture into water and extracting it with ether. That from *p*-methoxybenzylidenebenzylamine (Found : C, 79·0 ; H, 6·8%), on hydrolysis as already described, gave a basic fraction which yielded mainly benzylamine picrate together with a small amount of *p*-methoxybenzylamine picrate, and a neutral (aldehydic) fraction, which on oxidation with cold 3% permanganate gave *p*-anisic acid, from which a little benzoic acid was separated by sublimation. The product from benzylidene-*p*-methoxybenzylamine (Found : C, 80·1 ; H, 6·8%) behaved similarly.

Determination of the Equilibrium.—Preliminary experiments with artificial mixtures of the azomethines led to two methods by which their proportions could be estimated with fair accuracy. The first depends essentially on an estimation of the methoxyl content of the mixture of acids obtained as described above. After hydrolysis of the original mixture of azomethines, the aldehydes are isolated by extraction with ether and, after partial removal of the solvent under a long column, oxidised to the acids, which are extracted from the acidified solution with ether after dissolution of the oxides of manganese by the passage of sulphur dioxide. The second method (which on the whole is to be preferred, since it avoids the difficulty of freeing from solvent without loss mixtures containing so volatile a substance as benzoic acid) consists in converting the mixed aldehydes into their semicarbazones and estimating the methoxyl content in the latter, due correction being applied for the solubilities of the semicarbazones in the medium (100 c.c. of 2·5% aqueous ethyl alcohol containing 0·05 g. of free semicarbazide carbonate) from which they are precipitated. (The medium referred to was found to contain 0·0615 g. of benzaldehydesemicarbazone and 0·1102 g. of *p*-anisaldehydesemicarbazone unprecipitated.) A third method employing the mixed bases was found to be less expeditious and accurate than either of the above processes, and was therefore not developed. The following results

relate to products of interconversion obtained under the conditions specified in the preceding paragraph (*p*-methoxybenzylidenebenzylamine = I, benzylidene-*p*-methoxybenzylamine = II):

Isomeride used.	Substances analysed.	Conversion (%).	MeO-Compound by Zeisel. Wt. %, uncorr.	Wt. %, corr.	Mols. %.	Percentage of I.
I	Semicarbazones	98·6	81·1	82·3	79·7	79·7
II	,,	96·6	79·1	80·4	77·7	78·0
II	,,	97·2	78·0	79·4	76·5	
II	Acids	98·2	83·1		79·8	

The mean percentage of I, namely 78·9%, is recorded in the introduction as the percentage at equilibrium. The equilibrium ratio $k_{(I \rightarrow II)}/k_{(II \rightarrow I)}$ is 21·1/78·9 = 0·268.

Action of Alkali on Methylenebenzylamine and Benzylidenemethylamine.—Methylenebenzylamine, obtained by dehydration of benzylaminomethyl alcohol (Henry, *Ber.*, 1895, **28**, 924) over sulphuric acid in a vacuum and crystallised from ligroin, had m. p. 48° (Henry, *loc. cit.*, records 43°). It was stable to boiling aqueous alkali and boiling 1·46*N*- and 2·92*N*-alcoholic sodium ethoxide, and was hydrolysed by hot 2*N*-sulphuric acid to formaldehyde and benzylamine but no benzaldehyde. Fusion with potassium hydroxide at 300°, and heating with 1·45*N*-alcoholic sodium ethoxide at 190° for 7 hours, yielded nearly colourless oils which on hydrolysis with mineral acids gave formaldehyde (qualitative tests), benzaldehyde (about 10% of semicarbazone), benzylamine (picrate, chloroplatinate), and a very volatile base (small quantity). These results indicate a partial conversion into benzylidenemethylamine by potassium hydroxide and sodium ethoxide at the temperatures employed.

Benzylidenemethylamine prepared by Zaunschirm's method (*Annalen*, 1888, **245**, 281) contained benzaldehyde which could not be removed by distillation. Since treatment with aqueous semicarbazide acetate and sodium hydrogen sulphite brought about hydrolysis of the azomethine, the crude product was treated with an excess of hydroxylamine in 10% aqueous sodium hydroxide. Distillation of the residue from the ethereal extract yielded the pure azomethine as a colourless oil, b. p. 90—91°/30 mm. Experiments parallel with those indicated in the preceding paragraph yielded no evidence of conversion into methylenebenzylamine in the presence of hot alkali.

We wish to thank the Chemical Society and the Royal Society for grants in aid of this investigation.

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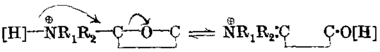
CLX.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part IV. Further Evidence relating to the Mechanism of Acid Catalysis in the Mutarotation of Nitrogen Derivatives of Tetra-acetylglucose.*

By John William Baker.

In Part II (J., 1928, 1583) two types of catalyst for the mutarotation of certain nitrogen derivatives of sugars were recognised: (i) those which attack the ionising proton directly, and (ii) those which facilitate its liberation indirectly, this class including strong acids. Since tetra-acetylglucosidylmethylanilide, in which the mobile hydrogen of the tautomeric system [H]—NR—C—O—C ⇌ NR=C C·O[H] has been replaced by a methyl group, could not be induced to exhibit mutarotation even in the presence of considerable concentrations of hydrochloric acid, it was concluded that for such weak bases the attack of the catalyst involves, not actual *co-ordination of the acid proton*, but merely *the augmentation*, by an electrostatic mechanism, of the positive field in the region of the electrons binding the original (mobile) hydrogen atom. It was considered possible, however (*loc. cit.*, p. 1586), that in the case of derivatives of very strong bases such actual co-ordination of the catalyst proton might occur. The resulting salt might thus have acquired the necessary mobile hydrogen and exhibit mutarotation consequent on the equilibration of the kationic system.



α- and β-forms.

In order to test this possibility various tetra-acetylglucosidyl derivatives of the type required have been prepared by the action of tetra-acetylglucosidyl bromide on strong secondary bases, which include various *p*-substituted benzylmethylamines, dimethyl- and diethyl-amines and piperidine. The hydrochlorides of these sugar derivatives have been isolated in a crystalline condition, and their solutions in absolute or 90% alcohol do in fact exhibit a change in rotation in accordance with the kinetics of unimolecular reaction. This change, however, does not appear to be due to the interconversion of the α- and β-forms, but to slow fission of the derivative into the parent tetra-acetylglucose and the hydrochloride of the

secondary base. A similar phenomenon is observed when the free sugar derivatives are examined in ethyl acetate solution in the presence of a little hydrochloric acid as a catalyst, and in these cases slow crystallisation of the base hydrochloride from the solution occurs in the polarimeter tube. On the basis of these negative results it seems probable, therefore, that for mutarotation, dependent on simple isomeric change, to be possible, the original sugar derivative itself (as distinct from its kation) must contain a separable hydrogen atom as was originally postulated by Baker, Ingold, and Thorpe (J., 1924, **125**, 268).

EXPERIMENTAL.

Preparation of p-*Substituted Benzylmethylamines*.—A mixture of 21 g. of the appropriate *p*-substituted benzyl bromide, 40 c.c. of 33% aqueous methylamine solution, and 200 c.c. of alcohol was warmed at 30—40° for 1 hour. Most of the alcohol was then distilled off, the residue was poured into dilute sodium hydroxide solution and shaken with ether, and the bases were extracted from the ethereal solution by dilute hydrochloric acid, recovered by means of ether from the basified extract, dried over anhydrous potassium carbonate, and, after removal of the ether, fractionated under reduced pressure; the monobenzylmethylamine distilled first (yield, 6—7 g.) and then, at a much higher temperature, the dibenzylmethylamine, which was not generally further purified. The secondary bases were purified and characterised in the form of their hydrobromides.

p-Methylbenzylmethylamine has b. p. 84°/6 mm. The *hydrobromide* separates from alcohol–ligroin in glistening plates, m. p. 166° (Found : Br, 36·9. $C_9H_{13}N,HBr$ requires Br, 37·0%).

p-Chlorobenzylmethylamine has b. p. 101°/5 mm. The *hydrobromide* crystallises from absolute alcohol in feathery clusters of thin square plates, m. p. 196° (Found : Br, 34·0. $C_8H_{10}NCl,HBr$ requires Br, 33·8%).

p-Cyanobenzylmethylamine has b. p. 143°/6 mm. The *hydrobromide* crystallises from absolute alcohol in clusters of fine needles, m. p. 209—210° (Found : Br, 35·3. $C_9H_{10}N_2,HBr$ requires Br, 35·3%).

Di(*p*-methylbenzyl)methylamine has b. p. about 180°/6 mm., and di(*p*-chlorobenzyl)methylamine b. p. about 200°/5 mm.

Di(*p*-cyanobenzyl)methylamine is left as a semi-solid residue after distillation of the *p*-cyanobenzylmethylamine. It crystallises from ligroin (b. p. 40—60°) in clusters of thin plates, m. p. 65°. The *hydrochloride*, crystallised from alcohol, has m. p. 250° (decomp.) (Found : Cl, 12·5. $C_{17}H_{15}N_3,HCl$ requires Cl, 11·9%).

Preparation of Tetra-acetylglucosidyl Derivatives of Various Secondary Bases.—Tetra-acetylglucosidyl bromide * (1 mol.) and the substituted benzylmethylamine (2 mols.) were gently warmed in ethereal solution until most of the ether had evaporated; the mixture was then left at the ordinary temperature for several hours. Separation of the hydrobromide of the base began almost immediately. The product was diluted with dry ether, the hydrobromide filtered off and washed with dry ether, the filtrate and washings extracted with 5% hydrochloric acid to remove any unchanged base, and the residue from the dried ethereal extract left to crystallise. The product from the *p*-cyano-derivative, which would not crystallise well, was converted into its hydrochloride by the action of hydrogen chloride in dry ether, and regenerated by the action of sodium carbonate solution. In the other cases the hydrochlorides were similarly prepared from the purified tetra-acetylglucosidylbenzylmethylamides.

The *benzylmethylamide*, crystallised from ether–ligroin, has m. p. 125° (Found: C, 58·5; H, 6·6. $C_{22}H_{29}O_9N$ requires C, 58·5; H, 6·5%). The *hydrochloride*, after crystallisation from a concentrated solution in ether–ligroin, has m. p. 80° (Found: Cl, 7·3. $C_{22}H_{29}O_9N,HCl$ requires Cl, 7·3%).

The p-*methylbenzylmethylamide* crystallises from ligroin (b. p. 60—80°), containing a little ether, in rosette clusters of fine needles, m. p. 99—100° (Found: C, 59·4; H, 6·5. $C_{23}H_{31}O_9N$ requires C, 59·3; H, 6·7%). The *hydrochloride* crystallises with difficulty from a concentrated solution in alcohol–ligroin (b. p. 60—80°); m. p. 175° (decomp.) (Found: Cl, 7·0. $C_{23}H_{31}O_9N,HCl$ requires Cl, 7·1%).

The p-*chlorobenzylmethylamide*, crystallised from ether–ligroin, has m. p. 104—105° (Found: C, 54·0; H, 5·7. $C_{22}H_{28}O_9NCl$ requires C, 54·3; H, 5·8%). The *hydrochloride* crystallises from alcohol–ligroin in clusters of fine needles, m. p. 137° (decomp.) (Found: ionisable Cl, 6·9. $C_{22}H_{28}O_9NCl,HCl$ requires ionisable Cl, 7·0%).

The p-*cyanobenzylmethylamide* crystallises from ether-ligroin in clumps of fine needles, m. p. 85—86° (Found: C, 57·7; H, 6·0. $C_{23}H_{28}O_9N_2$ requires C, 57·8; H, 5·9%). The *hydrochloride*, crystallised from hot alcohol, has m. p. 146° (decomp.) (Found: Cl, 7·1. $C_{23}H_{28}O_9N_2,HCl$ requires Cl, 6·9%).

Condensation of tetra-acetylglucosidyl bromide with piperidine yields two different products according to the experimental con-

* Tetra-acetylglucosidyl bromide (β-acetobromoglucose) is best purified by crystallisation from anhydrous ether. It may then be stored indefinitely over phosphoric oxide and a little potassium hydroxide in a vacuum.

ditions. (1) When 30 g. of tetra-acetylglucosidyl bromide are added to 50 c.c. of piperidine so that practically the whole dissolves before any considerable amount of action sets in, and the mixture is kept at 0—10°, a sudden vigorous reaction with much evolution of heat begins after a short period. At this stage a large volume of ether is rapidly added, the separated piperidine hydrobromide filtered off, and the product worked up as before. Addition of ligroin to the dried concentrated ethereal extract induces crystallisation (especially after seeding). The separated crystals (4·5 g.) are recrystallised from methyl alcohol–ligroin and then from ether containing a little methyl alcohol. The *piperidide* A was thus obtained in long thin prisms, m. p. 123° without decomposition. Decomposition slowly occurs in the fused substance (Found: C, 54·9; H, 7·1. $C_{19}H_{29}O_9N$ requires C, 54·9; H, 7·0%). The *hydrochloride* of this form crystallises from alcohol–ligroin in clusters of slender prisms, m. p. 126° (Found: Cl, 7·5. $C_{19}H_{29}O_9N,HCl$ requires Cl, 7·8%).

(2) When the tetra-acetylglucosidyl bromide is added slowly in 0·5 g. portions to the piperidine diluted with half its volume of ether, and the reaction mixture is kept cool in ice, separation of piperidine hydrobromide occurs slowly without rise in temperature. After the addition is completed the mixture is left in ice for 1 hour and then at the ordinary temperature for 3 hours. Since the form obtained under these conditions is much less soluble in ether, it is filtered off, mixed with piperidine hydrobromide, after dilution of the reaction mixture with dry ether. After removal of the piperidine hydrobromide with water the *piperidide* B crystallises from methyl alcohol–ligroin or ethyl acetate–ligroin in fine needles, m. p. 136° (decomp.) with previous slight darkening (Found: C, 54·9; H, 7·1%). A mixture of the two forms softens and darkens at 120—123°, but fusion (with decomposition) is not complete until 136°. The *hydrochloride* of the second form is unstable. Rapid crystallisation from the smallest possible volume of alcohol–ligroin yields large prisms, m. p. 130—131° (decomp.) (Found: Cl, 8·7%), but slower crystallisation yields a much more soluble product obtained only as a crystalline powder, m. p. 126—127° (Found: Cl, 12·4. The deacetylated derivative $C_{11}H_{21}O_5N,HCl$ requires Cl, 12·5%).

The Diethylamide.—Tetra-acetylglucosidyl bromide (10 g.) was added in small portions to 10 g. of anhydrous diethylamine at 30—40°. The reaction mixture was kept at the ordinary temperature until separation of the diethylamine hydrobromide was complete. The crude diethylamide was isolated in the usual manner as a yellow viscous gum which, since it could not be induced to crystallise, was converted directly into its hydrochloride by the action of hydrogen

chloride in dry ether. The sticky solid *hydrochloride*, after being washed with ether and crystallised from ethyl acetate containing a little methyl alcohol, had m. p. 152—153° (Found : Cl, 8·3. $C_{18}H_{29}O_9N$,HCl requires Cl, 8·1%). The yield was very small.

The *dimethylamide hydrochloride*, obtained similarly, had m. p. 159—160° (decomp.) (Found : Cl, 8·7. $C_{16}H_{25}O_9N$,HCl requires Cl, 8·6%).

Fission of the Hydrochlorides of Tetra-acetylglucosidyldiaryl(alkyl)-amines.—(a) *In* 90% *alcohol at* 24·5°. Since examination of the residue after the change in rotation shows that fission has occurred, only summaries of the polarimetric results are recorded. The experimental details are the same as those recorded in previous parts of this series (*loc. cit.*).

Benzylmethylamide. Strength of solution, 1·196 g./100 c.c. Mean value of unimolecular *k* (6 observations), 6·5 hrs.$^{-1}$ (maximum, 6·8; minimum, 6·1). The residue obtained by evaporation of the solution in a vacuum at the ordinary temperature was triturated several times with dry ether to remove any tetra-acetyl glucose produced by hydrolysis. The insoluble residue without purification had m. p. 178—180° and contained Cl, 23·1 (Calc. for C_7H_7·NHMe,HCl : Cl, 22·5%).

p-*Chlorobenzylmethylamide.* Strength of solution, 0·726 g./100 c.c. Mean value of *k* (6 observations), 5·8 hrs.$^{-1}$ (maximum, 6·0; minimum, 5·4).

p-*Cyanobenzylmethylamide.* Strength of solution, 0·650 g./100 c.c. Mean value of *k* (9 observations), 2·46 hrs.$^{-1}$ (maximum, 2·98; minimum, 2·20). The residue obtained as previously described contained Cl, 20·9 (Calc. for CN·C_7H_6·NHMe,HCl : Cl, 19·4%).

p-*Methylbenzylmethylamide.* Strength of solution, 0·714 g./100 c.c. Mean value of *k* (6 observations), 13·3 hrs.$^{-1}$ (maximum, 14·1; minimum, 12·6).

Piperidide (A, m. p. 126°). Strength of solution, 0·836 g./100 c.c. Mean value of *k*, 12·8 hrs.$^{-1}$ (maximum, 14·3; minimum, 11·3).

Interconversion of the two forms could not be accomplished.

Dimethylamide. Strength of solution, 0·773 g./100 c.c. Fission is extremely rapid. Mean value of *k* (3 observations), approximately 32 hrs.$^{-1}$.

(b) *In absolute alcohol at* 24·5°. *Dimethylamide.* A solution containing 0·362 g./100 c.c. (this being the limit of its solubility) changed in rotation from $[\alpha]_{5461}$ − 15·1° to $[\alpha]_{5461}$ + 95° in 26 hours. The residue, worked up as previously described, contained Cl, 30·0 (Calc. for $C_{16}H_{25}O_9N$,HCl : Cl, 8·6. Calc. for $NHMe_2$,HCl : Cl, 43·5%), showing that fission was almost complete.

Benzylmethylamide. A solution containing 0·802 g./100 c.c.

changed from $[\alpha]_{5461}$ *— 4·4° to* $[\alpha]_{5461}$ *+ 29·4° in 24 hours (final* value, 54°). The residue after removal of the ether-soluble portion contained Cl, 23·9 (Calc. for C_7H_7·NHMe,HCl : Cl, 22·5%).

Mutarotation of Tetra-acetylglucosidyldiaryl(alkyl)amides in Ethyl Acetate containing Hydrochloric Acid at 24·5°.—Benzylmethylamide. A solution containing 0·902 g. of the amide and 0·687 g. of 22·5 wt.% hydrochloric acid (2 mols.) in 100 c.c. of dry acid-free ethyl acetate changed in rotation from $[\alpha]_{5461}$ − 13·3° to + 27·1° in 128 hours, whence the mean value of k is 0·036 hr.$^{-1}$. The residue, freed from the ether-soluble portion, contained Cl, 17·8 (Calc. for C_7H_7·NHMe,HCl : Cl, 22·5%), hence a large amount of fission had occurred.

p-*Chlorobenzylmethylamide.* A solution containing 0·971 g. of the *amide and 0·683 g. of 22·5 wt.% hydrochloric acid (2 mols.) in* 100 c.c. of ethyl acetate changed from $[\alpha]_{5461}$ − 10·8° to + 21·6° in 120 hours, whence the mean value of k is 0·052 hr.$^{-1}$. Some *p*-chlorobenzylmethylamine hydrochloride, m. p. 198—200° (Found: ionisable Cl, 18·2. Calc.: ionisable Cl, 18·5%), separated in the polarimeter tube.

The author desires to thank the Royal Society for a grant with the aid of which most of the expense of this investigation was met.

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CLXI.—*The Constitution of the Red Isomeride of Creatinine Picrate responsible for Jaffé's Colour Reaction.*

By WINSTON KENNAY ANSLOW and HAROLD KING.

IT was shown by Jaffé in 1886 (*Z. physiol. Chem.*, **10**, 399) that an intense red colour is produced when a solution of creatinine is treated with aqueous picric acid and then with caustic alkali. Although this reaction has been extensively used for the quantitative estimation of creatinine in biological fluids since Folin (*ibid.*, 1904, **41**, 223) made it the basis of a colorimetric method, it cannot be said that the chemistry underlying Jaffé's observation is at all understood. Greenwald (and Gross) have devoted considerable attention to this reaction and have discovered a number of facts of importance. They dismissed (*J. Biol. Chem.*, 1924, **59**, 601) the suggestion (Chapman, *Analyst*, 1909, **34**, 475) that the red colour was due to sodium salts of reduction products of picric acid (picramic acid, etc.) and produced evidence for the existence of a red " tautomeride " of

yellow creatinine picrate. The constitutional formula suggested by Greenwald (*J. Amer. Chem. Soc.*, 1925, **47**, 1440), however, is open to criticism.

By comparing the reaction of creatinine with that given by a number of its derivatives, Greenwald showed that the red colour was produced only by those derivatives in which a keto-enolic change was possible.

$$NH{:}C{<}{}^{NMe\cdot CH_2}_{NH-CO} \rightleftharpoons NH{:}C{<}{}^{NMe\cdot CH}_{NH-C\cdot OH}$$

Furthermore, Weise and Trop (*Z. physiol. Chem.*, 1928, **178**, 125) conclude from a study of the reaction of numerous other substances with alkaline picric acid that Jaffé's reaction for creatinine is but a special case of a general reaction for active methylene or methine groups. Any explanation of the reaction must, therefore, take cognisance of the necessity for the presence of a mobile hydrogen atom of acidic character.

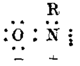
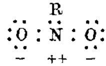
When the red alkaline solution of creatinine picrate was acidified, Greenwald and Gross, following on some earlier unpublished observations of S. R. Benedict and H. W. Banks, found that a red substance was precipitated which proved to be, on their interpretation, a "tautomeric" form of creatinine picrate. This could be changed by the application of heat into the yellow form of creatinine picrate. In a discussion of the conditions necessary for the production of the red colour, Greenwald (*loc. cit.*) assumed that creatinine or its substitutes function as bases, forming salts with picric acid. It is difficult to reconcile such an assumption with the observations that the red colour is only generated in alkaline solution and that it is given by non-basic substances such as malonic ester and ethyl acetoacetate.

The results of an investigation of Jaffé's reaction with which we have been engaged for some time confirm the existence of a red *isomeric* form of creatinine picrate and permit us to put forward a constitutional formula for this substance which is in agreement with the whole of the experimental evidence.

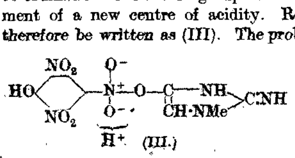
Red creatinine picrate may readily be prepared by the method to be described, a point of importance for obtaining a good yield being that acidification of the reaction mixture should be practically instantaneous. The product when freed from small amounts of uncombined picric acid by ether extraction is very sparingly soluble in water, readily soluble in sodium hydrogen carbonate solution, and is precipitated unchanged from the latter by mineral acids. It is not affected by contact with concentrated hydrochloric acid. It is, therefore, evident that the red alkaline solutions contain a red sodium salt of which red creatinine picrate is the free acid.

It is, indeed, possible to determine the number of points of acidity in the molecule by means of baryta. If red creatinine picrate be shaken with saturated baryta solution, in absence of carbon dioxide, it is converted into an insoluble scarlet barium salt. On analysis of the product the significant fact emerges that red creatinine picrate is a dibasic acid, and in presence of excess of baryta one acidic centre can form basic salts. Precisely similar results are obtained starting from a saturated solution of yellow creatinine picrate, containing yellow creatinine picrate in suspension. When treated with gradually increasing proportions of baryta, red barium salts of the same composition as those from red creatinine picrate are obtained.

In the light of the above facts, it is now possible to formulate red creatinine picrate and its salts. Since an alkaline solution of picric acid becomes deep red on addition of creatinine, it is unlikely that the phenolic group of the picric acid molecule is involved. Combination of picric acid and creatinine therefore takes place through the nitro-groups. The nitro-group contains normally one semi-polar double bond (I) and in its reactive phase two semi-polar double bonds (II) (compare Bennett and Willis, this vol., p. 258).

(I.)  and  (II.)

The anions of substances capable of keto-enol tautomerism and of substances containing reactive methylene groups are predominant in alkaline solution and will be attracted by the positively charged nitrogen atom in (I). The approach of the anion induces a greater degree of polarity as shown by the reactive phase of the nitro-group (II), with which co-ordination can then take place with consequent re-arrangement of charges. Alternatively, one might postulate an exiguous concentration of the reactive phase (II) as being present in solution in equilibrium with the normal form. Combination of creatinine and picric acid in alkaline solution thus takes place through co-ordination of the nitro-group with the enolic group and development of a new centre of acidity. Red creatinine picrate would therefore be written as (III). The problem as to which nitro-group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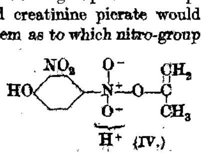

(IV.)

is involved with creatinine and which, if any, is present in quinonoid form (compare Hantzsch, *Ber.*, 1906, 39, 1084) with caustic alkali

remains undecided. It is of interest that two sodium salts, one containing 1 molecule of creatinine, 1 of picric acid and 2 of sodium hydroxide, the other, 2 molecules of creatinine, 1 of picric acid and 3 of sodium hydroxide have been prepared by Greenwald (*J. Biol. Chem.*, 1928, **77**, 539; 1928, **80**, 104) and fit in with the above formulation of the red acid. The presence of three nitro-groups in picric acid would allow of the addition of at least two molecules of creatinine in the way formulated above, and the compound formed would require 3 atoms of sodium as found by Greenwald.

In support of our formulation we may adduce an important observation of Reissert (*Ber.*, 1904, **37**, 837) which has now been followed up. When a solution of sodium ethoxide is added to an acetone solution of 2 : 4-dinitrophenol, the solution becomes red and if sufficiently concentrated deposits a brick-red sodium salt. When an aqueous solution of this salt is acidified with acetic acid, an intense violet-red colour is produced which is stable for some minutes, but if acidified with hydrochloric acid only a transient colour change occurs. We have prepared this sodium salt and find that under the most favourable conditions it consists of a mixture of 15·5% of the sodium salt of dinitrophenol with 84·5% of the disodium salt of an addition compound of acetone with dinitrophenol. The formulation (IV) of the additive compound is exactly analogous to that of red creatinine picrate.

When the disodium salt is acidified, the intense colour produced is evidently that of the unstable dibasic acid liberated.

Greenwald and Gross comment on the fact that picric acid cannot be replaced in Jaffé's reaction by other nitrophenols. Contrary, however, to the observations of these authors, we find that addition of creatinine to alkaline solutions of 2 : 4-dinitrophenol and of 3-methylpicric acid gives orange-red solutions, although in contradistinction to the reaction with picric acid a few minutes are required for the colour to develop. Furthermore, when alkaline solutions of 2 : 4-dinitrophenol, 2 : 6-dinitrophenol, 3-methylpicric acid, and 2 : 4-dinitro-1-naphthol-7-sulphonic acid containing creatinine are gradually treated with *N*-hydrochloric acid, they each give a transient red colour which at neutrality pervades the whole fluid and is temporarily stable, but disappears on addition of excess of acid. The colour cannot be reproduced by approaching the reaction mixture from the acid side. Ionisation of the enolic form or ionisation of the reactive methylene compound is an essential preliminary to formation of the co-ordination complex, and this condition is most readily attained by salt formation in alkaline solution.

EXPERIMENTAL.

Preparation of Red Creatinine Picrate.—A solution of picric acid (10 g.; 1 mol.) in boiling water (200 c.c.) was added to a solution of creatinine (5 g.; 1 mol.) in 50 c.c. of water. When cold, the solution, containing yellow creatinine picrate in suspension, was made alkaline with 50 c.c. of 2*N*-sodium hydroxide solution. The resultant deep red solution was cooled in ice and before crystallisation of sodium picrate had begun 50 c.c. of concentrated hydrochloric acid were added all at once with vigorous stirring. (Slow addition of acid gives a mixture of yellow and red precipitates which may finally be entirely yellow.) The red precipitate was collected and washed free from chlorides. When dry it weighed 8·6 g. and after removal of a small amount of picric acid by extraction in a Soxhlet extractor with ether, it weighed 7·1 g. When so prepared, "red" creatinine picrate is a carmine-coloured powder, and is definitely crystalline and anisotropic. When heated in a capillary tube, it turns yellow between 160° and 170° and then melts in the neighbourhood of 213°. Pure yellow creatinine picrate melts at 220—221° (Found: loss at 120°, 4·5; picric acid by nitron, 63·7. $C_4H_7ON_3,C_6H_3O_7N_3,H_2O$ requires H_2O, 5·0; picric acid, 63·6%).

The effect on the yield of varying the initial relative proportion of creatinine and picric acid is shown in the following table. The yield in each case is that obtained from 1 g. of creatinine.

Creatinine/picric acid	2 : 1	1 : 1	1 : 1·5	1 : 2	1 : 2·5
Yield of precipitate (g.)	0·7	1·7	1·8	3·1	3·9
Yield after ether extraction (g.)	0·65	1·3	1·1	1·1	1·3
Loss at 120°, %	1·7	2·8	1·5	4·4	4·3
% Picric acid on anhydrous solid	66·3	66·2	66·6	66·6	66·7

($C_4H_7ON_3,C_6H_3O_7N_3$ requires picric acid, 66·9%).

From this table it is clear that the proportion recommended by Greenwald, 1 mol. of creatinine to 2½ mols. of picric acid shown in the last column, possesses no advantage over the proportion recommended by us as shown in the second column. The use of excess of picric acid results in an increased weight of precipitate, but most of this is free picric acid which has to be removed by prolonged ether extraction.

Conversion of Red into Yellow Creatinine Picrate.—Red creatinine picrate (0·53 g.) was boiled with water (17 c.c.) until a clear yellow solution was obtained. On cooling, pale yellow needles (0·44 g.) of yellow creatinine picrate were obtained as was shown by m. p., crystalline form and analysis (Found: picric acid, 66·7. Calc.: 66·9%). This property of forming a clear yellow solution on boiling with water was made use of for the estimation of the picric acid

content of red creatinine picrate. Once in solution, precipitation by nitron was carried out in the usual way.

Red Barium Creatinine Picrates.—The calculated amount of saturated, standard baryta solution (0·4 N) free from carbonate was added to very finely powdered red creatinine picrate in a stoppered vessel, and the mixture shaken for ½ hour. The product, a scarlet solid, was rapidly filtered off and then quickly transferred to porous plate without washing so as to avoid possible hydrolysis. It was then dried in a vacuum.

For analysis of these salts, the barium compound was dissolved in boiling water, dilute sulphuric acid added, and the barium sulphate collected and weighed. Picric acid was then determined in the filtrate by nitron. Nitrogen was determined by Kjeldahl's method after preliminary reduction of the nitro-groups with tin and hydrochloric acid.

The following table shows the results of analysis of the products obtained when red creatinine picrate was treated in the manner described with increasing amounts of baryta.

Picrate/Baryta.	% Loss at 120°.	% Ba.	% Picric acid.	% N.	Ba : Picric acid : N.
1 : 1	15·6	24·0	37·3	13·7	1·07 : 1 : 5·99
1 : 1·1	14·8	25·5	35·5	12·5	1·2 : 1 : 5·76
1 : 1·5	14·7	29·3	33·6	12·7	1·45 : 1 : 6·18
1 : 1·65	14·3	29·8	29·7	11·8	1·67 : 1 : 6·49
1 : 2·75	15·2	31·2	30·0	11·4	1·73 : 1 : 6·2

[Calc. for the normal salt, $(C_{10}H_8O_8N_6)_2Ba_2,14H_2O$: H_2O, 20·9; Ba, 22·8; N, 13·9; picric acid, 37·9%. Calc. for the basic salt,

$(C_{10}H_8O_8N_6)_2,Ba_3(OH)_2,20H_2O$:

H_2O, 24·2; Ba, 27·7; N, 11·3; picric acid, 30·8%.]

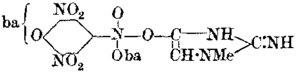
When yellow creatinine picrate was used in exactly the same way instead of red creatinine picrate, the results obtained were very similar and are shown in the following table:

Picrate/Baryta.	% Loss at 120°.	% Ba.	% Picric acid.	% N.	Ba : Picric acid : N.
1 : 1	13·3	26·9	39·0	13·4	1·16 : 1 : 5·61
1 : 1·5	14·1	29·5	35·0	12·0	1·4 : 1 : 6·07
1 : 2	18·8	28·4	27·7	10·3	1·71 : 1 : 6·13
1 : 2·5	15·3	32·3	31·4	11·5	1·71 : 1 : 6·00

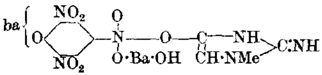
A study of these two tables, particularly the columns involving ratios, shows that red barium creatinine picrate is the barium salt of a dibasic acid. In the first row in both tables, where the baryta and creatinine picrate (red or yellow) are used in equimolecular proportion, the whole of the available barium is fixed and is equivalent to two acidic centres. Whatever excess of baryta is used, the barium fixed only rises very slightly above three equivalents. The high barium ratios found for the salts of highest barium content,

namely, 1·7 instead of 1·5, is explained by the difficulty of removing adhering baryta by the method of preparation employed. For this reason the analytical figures for barium are probably slightly high in every case.

The simplest interpretation of these results is that in the presence of two equivalents of baryta a normal barium salt is formed of the following formula, whereas in presence of excess of baryta a partly



basic salt is formed of the following formula :



When red barium creatinine picrate (1·0 g.) was ground with concentrated hydrochloric acid (5 c.c.), red creatinine picrate was liberated (yield, 0·25 g.). On heating in a capillary tube, it became yellow at about 150° and melted at about 209°. A mixture with red creatinine picrate melted at 211°.

Action of Sodium Ethoxide on 2 : 4-Dinitrophenol in Presence of Acetone.—2 : 4-Dinitrophenol (2 g.) was dissolved in a mixture of absolute alcohol (50 c.c.) and acetone (25 c.c.). The addition of sodium ethoxide solution (from 2·5 g. of sodium in 50 c.c. of alcohol) produced a deep red solution and in a few seconds this was followed by separation of a brick-red precipitate. This was collected, washed with absolute alcohol and ether, and dried in a vacuum (yield, 3·19 g.). The substance has no m. p. and explodes on heating. When dissolved in dilute sulphuric acid and extracted with ether, it gave a good yield of unchanged dinitrophenol, and when a small quantity was dissolved in dilute sulphuric acid and distilled, the first few drops of distillate had the odour of acetone and gave Legal's test.

On analysis the product proved to be mainly the disodium salt of acetone-dinitrophenol mixed with a small proportion of sodium dinitrophenoxide. Attempts to prepare a product uncontaminated with the latter salt were unsuccessful (Found : Na, 14·2; N, 8·8; acetone by Messinger's method, 15·4, whence ratio Na : N : acetone is 0·98 : 1 : 0·42. Calc. for a 84·5% mixture of $C_6H_3O_5N_2Na,C_3H_5ONa$ and 15·5% of $C_6H_3O_5N_2Na$, the whole containing 10% of moisture : Na, 13·8; N, 9·3; acetone, 15·4%).

NATIONAL INSTITUTE FOR MEDICAL RESEARCH,
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CLXII.—*Acid and Salt Effects in Catalysed Reactions. Part XX. The Ionisation of Acids in Salt Solutions.*

By Harry Medforth Dawson and William Lowson.

The methods which have been used for the determination of the degree of ionisation of acids in accordance with the classical ionic theory depend on measurements of electrical conductivity, freezing-point change, potential difference and reaction velocity. Such observations continue to provide the necessary data, although the method of interpretation has been modified in all cases by recent theoretical developments.

The most widely used method is, of course, the conductivity method and it is probable that this yields substantially correct results if its application is restricted to dilute solutions of the weaker acids. When salt solutions are substituted for water as the solvent medium, the conductivity method fails for obvious reasons, and in these circumstances it is necessary to look for other methods which may permit of the determination of the degree of ionisation of acids. The present paper gives an account of an attempt to derive the required hydrogen-ion concentration (as distinguished from the hydrogen-ion activity) from reaction velocity data and to ascertain the influence of the concentration of the salt solution on the ionisation constants of acids.

In general, the application of this method must take account of the fact that catalytic effects may be produced by both positive and negative ions and by neutral molecules and that the magnitudes of the coefficients which characterise the various catalytic entities vary with the nature of the reaction medium. If the catalysed reaction and the salt solution in question are such that the only measurable catalytic effects are those due to the acid under investigation, the equation for the specific reaction velocity may be written

$$v = v_h + v_a + v_m = k_h[H^+] + k_a[A^-] + k_m[HA] \quad . \quad (1)$$

in which the coefficients k_h, k_a, and k_m depend on the nature and concentration of the salt solution. Since $[H^+] = [A^-]$ and $[HA] = c - [H^+]$, where c is the concentration of the acid, the above equation may be written

$$[H^+] = (v - k_m c)/(k_h + k_a - k_m) \quad . \quad . \quad . \quad (1A)$$

The experimental data to which this equation is now applied have reference to the rate of hydrolysis of ethyl acetate in sodium chloride solutions (0—4 moles per litre) with acetic, glycollic, chloroacetic

and dichloroacetic acids as catalyst. One of the advantages attaching to the study of this particular reaction is that the coefficients k_a and k_m have for the most part such small values that they can be neglected in comparison with k_h. In other words we are mainly concerned with hydrogen-ion catalysis.

In the application of equation (1A) it is assumed that hydrochloric acid is completely ionised in the sodium chloride solutions and that observations made with this acid (0·01*N*) afford therefore a measure of k_h. If this assumption is valid, it follows that the reaction velocity data for the other acids will not be disturbed to any measurable extent by the interaction of hydrogen ion with chlorine ion even when the ratio $[Cl^-]/[H^+]$ is of the order 10^3—10^4. The absence of such interference is obviously dependent on the ionisation constant of hydrochloric acid and the order of magnitude of this would appear to be very uncertain. The value $K = 10^6$ is given by Schreiner (*Z. physikal. Chem.*, 1924, **111**, 419) and $K = 10^7$ by Ebert (*Naturwiss.*, 1925, **13**, 393). On the other hand, the electrical conductivities of very dilute solutions of hydrochloric acid might suggest that it is much smaller. In these circumstances, it is necessary to consider the possibility that the reaction velocity data, more particularly in the case of concentrated sodium chloride solutions, may be measurably affected by the formation of undissociated hydrochloric acid, for this may be confidently expected to be an extremely active catalytic agent.

If the solvent for the acids under investigation is a concentrated solution containing x mols. of sodium chloride per litre, and if such solutions contain undissociated hydrochloric acid, the relation between [HCl] and $[H^+]$ is given by $[HCl] = x[H^+]/K$ and the specific reaction velocity for a solution of hydrochloric acid by

$$v = k_h[H^+] + k_m[HCl] = k_h[H^+](1 + k_m x/k_h K) \quad . \quad (2)$$

For the corresponding solution of any other acid HA, account must be taken of the equilibria $HA \rightleftharpoons H^+ + A^-$ and $H^+ + Cl^- \rightleftharpoons HCl$, and it is evident that the formation of undissociated hydrochloric acid will lead to a hydrogen-ion concentration smaller than that which would have been obtained in the absence of interaction between the hydrogen and chlorine ions. The specific reaction velocity for this solution is given by

$$v = k_h[H^+](1 + k_m x/k_h K) + k_a[A^-] + k_m[HA] \quad . \quad (3)$$

in which $[H^+]$ is less than $[A^-]$. If the second and third terms in equation (3) can be neglected, or alternatively evaluated, it is apparent that the combination of equations (2) and (3) would permit us to derive the relative hydrogen-ion concentrations of the two

solutions, but does not enable us to determine the ionisation constant of the acid HA. This, indeed, cannot be obtained from the reaction velocity data unless the formation of undissociated hydrochloric acid is stoicheiometrically and catalytically negligible. Since $[HCl] = x[H^+]/K$ and the maximum value of x is about 5, it follows that the stoicheiometric effect will be negligible if K is greater than about 10^3 and that the catalytic effect will be negligible if k_m/k_hK is less than about 10^{-3}. In this connexion it is important to recognise that k_m/k_h is a function of K. According to Brönsted (*Trans. Faraday Soc.*, 1928, **24**, 630) these quantities are connected by an equation of the form $k_m/k_h = aK^n$, where a and n are constants which depend on the nature of the catalysed reaction and $n > 0 < 1$. Since this relation is used by us in an attempt to show that k_m/k_hK is negligibly small, attention may be directed to the values of k_m and K which have been derived for a series of acids from catalytic observations on the acetone–iodine reaction (Dawson, Hall, and Key, J., 1928, 2844). By plotting log k_m against log K, a straight line is obtained, and from this constants are derived which lead to the equation $k_m = 0{\cdot}0014K^{0{\cdot}64}$, or since $k_h = 4{\cdot}65 \times 10^{-4}$, to $k_m/k_h = 3{\cdot}00\ K^{0{\cdot}64}$. The values of k_m calculated from this equation are in close agreement with the values derived from the experimental data, as may be seen from Table I, in which the first row of figures gives the values of K, the second gives the observed values of k_m, and the third the calculated values.

TABLE I.

Acid	Propionic	Acetic	β-Chloro-propionic	Glycollic	Chloro-acetic	Dichloro-acetic
K	$1{\cdot}38 \times 10^{-5}$	$1{\cdot}85 \times 10^{-5}$	$1{\cdot}01 \times 10^{-4}$	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}51 \times 10^{-3}$	$5{\cdot}0 \times 10^{-2}$
$k_m \cdot 10^6$ obs. ...	1·1	1·35	3·7	5·7	22·2	200
$k_m \cdot 10^6$ calc. ...	1·09	1·31	3·83	5·0	22·0	206

Within limits which are represented by a variation of the ionisation constant in the ratio 1 : 4000, it is evident from the above table that the relation between k_m/k_h and K can be accurately represented by an equation of the type $k_m/k_h = aK^n$. An equation of this type, namely, $k_m/k_h = K^{0{\cdot}5}$, was first suggested by Taylor (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 37) as the result of observations on the hydrolysis of ethyl acetate. In view of the limited scope of those experiments it is probable that the value assigned to the exponent n is not very exact. Brönsted's observations on the mutarotation of glucose (*loc. cit.*) may be expressed by the equation $k_m/k_h = 0{\cdot}4\ K^{0{\cdot}4}$ and are of particular importance for our purpose in that they show that this type of equation is valid over an ex-

tremely wide range of K values. Further confirmation of its validity has been provided by observations on the hydrolysis of ethyl orthoacetate, orthopropionate and orthocarbonate (Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, 1929, **25**, 59). There is thus very substantial evidence for the general applicability of the relation $k_m/k_h = aK^n$.

When this value for k_m/k_h is introduced into the expression k_mx/k_hK which affords a measure of the relative catalytic effect produced by undissociated hydrochloric acid (compare equation 2), this becomes ax/K^{1-n}, in which x and K are determined by the strength of the sodium chloride solution, whilst a and $(1-n)$ depend on the nature of the catalysed reaction. The available evidence indicates that a does not differ greatly from unity and that $(1-n)$ is a positive quantity less than unity. From this it follows that, if a solution of hydrochloric acid in sodium chloride (*e.g.*, $0{\cdot}01N$-HCl + $1{\cdot}0N$-NaCl) contains a catalytically effective quantity of undissociated acid, the effect of the latter may be expected to vary with the catalysed reaction. Experiment shows, however, that the change in the reaction velocity produced by the addition of sodium chloride is within narrow limits the same for different reactions; for example, sucrose inversion, ester hydrolysis, and the keto-enol change of acetone. This constancy of the salt effect would seem to show conclusively that undissociated hydrochloric acid is not responsible for any appreciable catalytic effect. Since the relative magnitude of this effect is represented by a/K^{1-n}, it may be inferred that the ionisation constant of hydrochloric acid is very large, possibly not less than the values suggested by Schreiner and Ebert (*loc. cit.*). It follows further that the reaction velocity data obtained for the various acids in solutions of sodium chloride may be applied to the derivation of the required hydrogen-ion concentrations by the use of equation (1A).

A further point to which attention may be directed is that the interpretation of the reaction velocity data does not involve any assumption which necessarily distinguishes between the activities and the concentrations of the reacting substances. If for the sake of simplicity we confine our attention to the action of one of the catalytic entities, namely, the hydrogen ion, and suppose that the rate of hydrolysis is determined by the respective activities, we may write

$$v = k_h a_H a_e a_w = k_h f_h[\mathrm{H}^+]f_e[\mathrm{ester}]f_w[\mathrm{H_2O}]$$

and since the ester concentration is constant and the values of k_h, f_h, f_e, f_w and $[\mathrm{H_2O}]$ are determined by the concentration of the sodium chloride, it follows that the above equation reduces in

general to the form represented by the term for the action of the hydrogen ion in equation (1). Rigid adherence to the concept of ionic strength might suggest that this is not strictly true in the case of the more dilute salt solutions containing the stronger acids, but the behaviour of such solutions does not suggest any need for differentiation.

Before proceeding to the description of the results obtained with the different acids, it should be mentioned that the actual procedure varies somewhat with the strength of the catalysing acid. With acetic acid, the auto-catalytic effect must be taken into account, and with dichloroacetic acid the catalytic influence of the undissociated acid is very appreciable.

If, in the case of acetic acid, the original concentrations of the ester and of the acid are denoted by a and b respectively, that of the acetic acid formed by y, then, since $[H^+] = \sqrt{K(b + y)}$, we may write

$$dy/dt = k_h[H^+][\text{ester}][H_2O] = k'_h\sqrt{K}(a - y)(b + y)^{\frac{1}{2}}$$

which on integration gives

$$k'_h\sqrt{K} = \frac{1}{t\sqrt{a + b}}\left\{\log\frac{\sqrt{a + b} + \sqrt{b + y}}{\sqrt{a + b} - \sqrt{b + y}} - \log\frac{\sqrt{a + b} + \sqrt{b}}{\sqrt{a + b} - \sqrt{b}}\right\} \quad (4)$$

where $k'_h\sqrt{K}$ represents the specific catalytic effect of the acetic acid. For a given salt solution, k'_h is given by the data for hydrochloric acid (Dawson and Lowson, this vol., p. 393), whence K is derived from $K = (k'_h\sqrt{K}/k'_h)^2$.

In the experiments with glycollic, chloroacetic and dichloroacetic acids the auto-catalytic effect of the acetic acid produced may be neglected, and in these circumstances the reaction velocity for unit ester concentration is given by $v = 1/t \,.\, \log_e a/a - y$. This velocity is entirely due to the hydrogen ion when glycollic acid is used. With chloroacetic acid, a slight effect is attributable to the undissociated acid, and this is quite appreciable in the case of dichloroacetic acid. In order to determine the value of k_m for dichloroacetic acid, the procedure described by Dawson, Hall, and Key (*loc. cit.*) has been followed. To what extent the value of k_m obtained in this way is affected by the salt concentration is uncertain but it may readily be shown that such variations in k_m are not of much importance in the present connexion.

On the assumption that K for salt-free solutions of dichloroacetic acid is equal to $5{\cdot}0 \times 10^{-2}$, the value obtained by the method referred to is $k_m = 0{\cdot}8 \times 10^{-3}$. The following table shows that the observed reaction velocities for acid concentrations over the range $c = 0{\cdot}($

to $c = 0{\cdot}2$ are in close agreement with the values calculated from the equation

$$v = v_h + v_m = 6{\cdot}5 \times 10^{-3}[H^+] + 0{\cdot}8 \times 10^{-3}[HA] \quad . \quad (5)$$

The first and second rows give the concentration of the acid and of the hydrogen ion, the third and fourth the values of v_h and v_m, and the fifth and sixth show the calculated and observed velocities.

TABLE II.

Catalytic activity of dichloroacetic acid.

c	0·01	0·02	0·05	0·1	0·2
$[H^+]$	0·00854	0·0153	0·0309	0·0500	0·0780
$v_h \cdot 10^4$	0·555	0·995	2·01	3·25	5·07
$v_m \cdot 10^4$	0·012	0·037	0·15	0·40	0·98
$v \cdot 10^4$ cal.	0·567	1·03	2·16	3·65	6·05
$v \cdot 10^4$ obs.	0·564	1·04	2·16	3·78	5·93

The observed velocities are obviously closely reproduced by taking into account the catalytic activity of the undissociated acid, which, since $k_m/k_h = 0{\cdot}8/6{\cdot}5$, is about one-eighth as active as the hydrogen ion.

For the most part, reaction velocities were measured with an ester concentration of 20·0 c.c. per litre, but on account of salting-out effects this was reduced to 8·0 c.c. in the experiments with $3M$- and $4M$-salt solutions. This reduction in the ester concentration does not appreciably affect the velocity when hydrochloric acid is the catalyst, but a slight increase is observed in the case of the weaker acids. The increase does not, however, materially affect the relations shown by the numbers in the following tables. In the case of acetic acid (Table III) the data recorded are the sodium chloride concentration (x), the value of $k'_h\sqrt{K}$ given by equation (4), and the value of K. For glycollic acid (Table IV) and dichloroacetic acid (Table V) the data given are x, the velocity $v = 1/t \cdot \log_e a/a - y$, the hydrogen-ion concentration $[H^+]$, and the ionisation constant K. The corresponding data for chloroacetic acid were recorded in the preceding paper (*loc. cit.*), which also gives the values of k'_h derived from the experiments with hydrochloric acid.

TABLE III.

Ionisation of acetic acid (0·1N) *in sodium chloride solutions.*

x.	$k'_h\sqrt{K} \cdot 10^4$.	$K \cdot 10^5$.	x.	$k'_h\sqrt{K} \cdot 10^4$.	$K \cdot 10^5$.
0	0·269	1·71	0·50	0·397	2·94
0·01	0·285	1·91	1·0	0·423	2·70
0·04	0·308	2·20	2·0	0·439	1·96
0·10	0·331	2·46	3·0	0·444	1·41
0·30	0·367	2·77	4·0	0·400	0·81

TABLE IV.

Ionisation of glycollic acid (0·1N) in sodium chloride solutions.

x.	$v \,.\, 10^4$.	$[H^+] \,.\, 10^3$.	$K \,.\, 10^4$.	x.	$v \,.\, 10^4$.	$[H^+] \,.\, 10^3$.	$K \,.\, 10^4$.
0	0·255	3·92	1·60	0·3	0·350	5·01	2·64
0·01	0·262	4·02	1·68	0·5	0·372	5·08	2·71
0·02	0·271	4·15	1·80	1·0	0·410	5·04	2·67
0·03	0·278	4·24	1·88	2·0	0·450	4·55	2·17
0·04	0·285	4·34	1·97	3·0	0·492	4·17	1·81
0·10	0·307	4·61	2·23	4·0	0·480	3·40	1·20

TABLE V.

Ionisation of dichloroacetic acid (0·05N) in sodium chloride solutions.

x.	$v \,.\, 10^4$.	$[H^+] \,.\, 10^2$.	$K \,.\, 10^2$.	x	$v \,.\, 10^4$.	$[H^+] \,.\, 10^2$.	$K \,.\, 10^2$.
0	2·16	3·09	5·0	1·0	2·96	3·49	8·05
0·04	2·24	3·19	5·6	2·0	3·43	3·33	6·65
0·1	2·36	3·34	6·7	3·0	3·94	3·22	5·8
0·3	2·48	3·37	7·0	4·0	4·33	2·95	4·25
0·5	2·64	3·44	7·6				

From the above data and the corresponding numbers for chloroacetic acid it is apparent that the ionising tendency of the different acids is affected in the same manner by the added salt. As the salt concentration increases, the ionisation constant increases to a maximum and then decreases. There is indeed a close approximation in the behaviour of the different acids, as may be readily seen by comparing the values of $R_x = K_x/K_0$, where K_x is the ionisation constant in the x molar salt solution and K_0 the constant for the salt-free solution. The values of R_x are shown in Table VI.

TABLE VI.

Values of $R_x = K_x/K_0$ *in sodium chloride solutions.*

x.	$R_x(CH_3\cdot CO_2H)$.	$R_x(OH\cdot CH_2\cdot CO_2H)$.	$R_x(CH_2Cl\cdot CO_2H)$.*	$R_x(CHCl_2\cdot CO_2H)$.	R_x cal.
0	1	1	1	1	1
0·01	1·12	1·05	1·09	—	1·12
0·02	—	1·12	1·15	—	1·17
0·03	—	1·17	1·21	—	1·21
0·04	1·29	1·23	1·23	1·12	1·24
0·05	—	—	1·29	—	1·27
0·10	1·44	1·39	1·42	1·34	1·38
0·20	—	—	1·51	—	1·50
0·30	1·62	1·65	1·56	1·40	1·58
0·50	1·72	1·69	1·66	1·52	1·67
1·0	1·58	1·67	1·57	1·61	1·66
2·0	1·15	1·35	1·28	1·33	1·33
3·0	0·83	1·13	0·98	1·16	0·94
4·0	0·47	0·75	0·64	0·85	0·63

* The K_x values for chloroacetic acid recorded in the preceding paper have been slightly modified as the result of supplementary reaction velocity measurements; the resulting changes are not of any importance.

From this table it is apparent that the addition of sodium chloride raises the ionisation constant of the acid in all cases to a maximum

which is 60 to 70% greater than the constant for the salt-free solution and that this maximum is reached at a sodium chloride concentration which lies between 0·5 and 1·0 mol. per litre. In this connexion it may be noted that previous observations on the acetone–iodine reaction with acetic acid as catalyst in solutions of lithium, sodium and potassium chloride (Dawson and Key, J., 1928, 1239) have shown that the curves which represent the connexion between K_x and x are of the same type. The quantitative differences would seem to depend only on the nature of the ions of the inert salt.

Analysis of the R_x–x curve shows that it corresponds with an equation of the form $R_x = 10^{a\sqrt{x}-bx}$. Characteristic points on this curve are the maximum point ($R_x = R_m$, $x = x_m$) and the point ($R_x = 1$, $x = x_1$) at which the ionisation constant of the acid has the same value as in the salt-free solution.

The equation may be written

$$\log R_x = a\sqrt{x} - bx \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

whence $$d \log R_x = (\tfrac{1}{2}ax^{-\frac{1}{2}} - b)dx$$

and therefore $$R_x = R_m \text{ when } x = x_m = a^2/4b^2 \quad . \quad . \quad . \quad (7)$$

and $$\log R_m = a\sqrt{x_m} - bx_m = a^2/4b \quad . \quad . \quad . \quad . \quad (8)$$

Furthermore, it is evident that $R_x = 1$ when $a\sqrt{x} - bx = 0$, that is to say, when

$$x = 0 \text{ and } x = x_1 = a^2/b^2 \quad . \quad . \quad . \quad . \quad (9)$$

and by comparing equations (7) and (9) we obtain

$$x_1 = 4x_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

According to the last equation, the salt concentration at which the degree of ionisation of the acid is the same as in the salt-free solution is four times the concentration for which the ionisation is a maximum. Since the specific effects of the ions find expression in the constants a and b, it follows that this relation is independent of the nature of the inert salt.

On account of the flatness of the R_x–x curve in the neighbourhood of the maximum, it is not possible to determine x_m from the graph with any exactitude, but it may readily be shown that the data recorded in the present paper, as well as the results obtained for acetic acid in solutions of other alkali-metal chlorides (*loc. cit.*), are in approximate agreement with equation (10).

Since R_m and x_1 can be readily derived from the experimental curves, the values of these quantities may be utilised in the calculation of the constants a and b, which are given by the equations

$$a = 4 \log R_m/\sqrt{x_1} \text{ and } b = 4 \log R_m/x_1.$$

In accordance with the data of Table VI, the values assigned to these constants are $a = 0{\cdot}54$ and $b = 0{\cdot}32$. These correspond with $x_m = 0{\cdot}71$, $R_m = 1{\cdot}68$ and $x_1 = 2{\cdot}85$. The values of R_x calculated from $\log R_x = 0{\cdot}54\sqrt{x} - 0{\cdot}32x$ are shown in the last column, and when due consideration is given to the magnitude of the error * which may attach to the individual figures, it is apparent that this equation affords for the most part a satisfactory account of the experimental results. The most concentrated solutions must, however, be excepted and the differences shown by the various acids in the 4-molar salt solutions are such as to suggest that new specific effects, which vary with the nature of the acid, come into play at these large salt concentrations. In spite of this divergence, the important fact remains that the logarithmic formula reproduces fairly closely the observed relations for a series of acids with ionisation constants which vary in the ratio 1 : 3000 over a wide range of salt solutions. It is indeed possible that the applicability of this formula is not restricted by the magnitude of the ionisation constant.

The constant a affords a measure of the inert salt effect which is responsible for the initial increase in the ionisation constant, whilst b measures the effect responsible for the subsequent decrease. Since the observations relate to solutions of one and the same salt, the further consideration of the logarithmic formula will be limited to a comparison of the experimental results with the relation indicated by the Debye–Hückel theory.

Assuming that the ions concerned are univalent and adopting the usual symbols for activities, activity coefficients and ionic strengths, then, since

$$R_x = K_x/K_0 = K_x/K_a \,.\, K_a/K_0$$

or

$$\log R_x = \log K_x/K_a - \log K_0/K_a$$

it follows that a theoretical expression for $\log R_x$ may be obtained by evaluating K_x/K_a and K_0/K_a in terms of the interionic force theory.

We may write $\quad K_a = a_+a_-/a = f_+f_-/f \,.\, c_+c_-/c = K_x \,.\, f_\pm^2/f$

or $\quad \log K_x/K_a = \log f - 2 \log f_\pm$

and since $\quad -\log f_\pm = \alpha\sqrt{\mu} - \beta\mu$

and $\quad \log f = \gamma \,.\, \mu$

we obtain $\quad \log K_x/K_a = 2\alpha\sqrt{\mu} - \beta'\mu$ (11), where $\beta' = 2\beta - \gamma$.

The corresponding expression for $\log K_0/K_a$ may be written

$$\log K_0/K_a = 2\alpha\sqrt{\mu_0} - \beta''\mu_0$$

* In the case of dichloroacetic acid, which is 60—70% ionised, the probable error in K is increased by the circumstance that $[H^+]$ and $[HA]$ are both affected by an error in the measured reaction velocity.

where μ_0 is the ionic strength of the salt-free solution and β'' is in general different from β', and therefore

$$\log R_x = 2\alpha(\sqrt{\mu} - \sqrt{\mu_0}) - \beta'\mu + \beta''\mu_0 \quad . \quad . \quad (12)$$

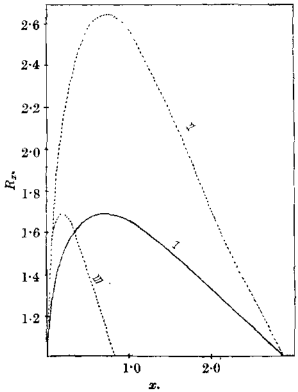
Comparison of this theoretical relation with equation (6) shows the existence of a difference at small salt concentrations in that the ratio $(\sqrt{\mu} - \sqrt{\mu_0})/\sqrt{x}$ varies with the salt concentration for a given acid ($\sqrt{\mu_0}$ = constant) and with the nature of the acid for a given salt concentration. Effective comparison of the R_x values for such dilute salt solutions would, however, necessitate greatly increased accuracy in the measurement of the reaction velocities and for this reason we shall confine our attention to the consideration of differences which are entirely outside the range of experimental errors. In this connexion it may be noted that the theoretical relation reduces to the form

$$\log R_x = 2\alpha\sqrt{x} - \beta' x \quad . \quad . \quad . \quad . \quad (13)$$

if the ionisation constant of the acid is sufficiently small. This equation is identical in form with the empirical formula (equation 6), and since the applicability of the latter does not depend on the ionisation constant of the acid, it would seem permissible to compare the general Debye–Hückel coefficient $2\alpha = 1{\cdot}0$ with the empirical coefficient $a = 0{\cdot}54$. The difference between these two numbers is very large and by equating either the x or R_x values which correspond with the observed maximum value of the ionisation constant, it may readily be shown that the larger coefficient is incompatible with the experimental R_x–x curves. If, for example, we combine the assumption that $a = 2\alpha = 1{\cdot}0$ with the fact that $K_x = K_0$ when the salt concentration is about 3 mols. per litre, then from equation (10), $x_1 = 4x_m = 3{\cdot}0$, we obtain $b = a/\sqrt{x_1} = 0{\cdot}58$, and from equation (8) $\log R_m = a^2/4b = 0{\cdot}43$ or $R_m = 2{\cdot}70$. The observed mean value of R_m is 1·68 and it follows that the observed maximum increase in the ionisation constant is only 68/170 or 40% of what would be anticipated on the assumption that $a = 2\alpha = 1{\cdot}0$. On the other hand, if we combine this assumption with the observation that $R_m = 1{\cdot}68$, then from equation (8) we derive $b = 1{\cdot}11$, and this in accordance with equation (9) leads to $x_1 = 0{\cdot}8$, whereas the mean observed value of x_1 is 3·0 mols. per litre. Since the percentage errors involved in the determination of R_m and x_1 are quite small, there is obviously a very considerable discrepancy between the results of these experiments and the conclusions which follow from the application of the interionic attraction theory to the problem. The differences in question, which are illustrated in the diagram, suggest that the value of α which determines the magnitude

of the mean activity coefficient $f_{\pm}$ of an acid in salt solutions is very much less than the value indicated by the Debye–Hückel theory.

A considerable amount of additional evidence might be cited in support of the view that the coefficient α is by no means independent of the nature of the ions concerned. The validity of the dilution law for the so-called transition acids, which is shown by the con-



Comparison of the R_x-x curves given by the experimental data with those derived from the application of the interionic attraction theory. Curve I corresponds with the experimental results given by $\log R_x = 0{\cdot}54\sqrt{x} - 0{\cdot}32x$; Curve II with the assumption that the maxima on the experimental and the theoretical curves coincide in respect of the salt concentration; Curve III with the assumption that the magnitudes of the observed and the theoretical maxima are identical.

stancy of $K_0 = c_+c_-/c$ at moderate dilutions, suggests very forcibly that the magnitude of the interionic force effect in such solutions is very small compared with that in corresponding solutions of salts. In agreement with this, it has been found that the catalytic activity of acids of widely different ionising tendency varies with the concentration in a manner which can be satisfactorily interpreted in terms of a fixed value of the ionisation constant (K_0). This value, which is independently derived from the catalytic observations, is, moreover, identical with that afforded by measurements

of the electrical conductivity of the acids in dilute solution (compare Dawson, Hall, and Key, *loc. cit.*).

Attempts have recently been made to derive a value for α from the conductivity data for certain organic acids (Davies, *Phil. Mag.*, 1927, **4**, 244). The numbers obtained vary from 0·35 for *o*-chlorobenzoic acid to 0·44 for 3 : 5-dinitrobenzoic acid, the mean value for seven acids being 0·38. According to Nonhebel (*ibid.*, 1926, **2**, 1085), the most probable value for hydrochloric acid deduced from *E.M.F.* measurements is $\alpha = 0{\cdot}39$. The close agreement may be accidental, for there can be little doubt that the accurate determination of α for acids on the basis of such data is attended by considerable difficulties. In the light of all the evidence there is, however, much to be said in support of the view that the value of α for acids is much less than the normal Debye–Hückel value. From this it would follow that the ionic strength hypothesis as expressed by the equation $-\log f_{\pm} = 0{\cdot}5\sqrt{\mu}$ is not applicable when $f_{\pm}$ refers to an acid electrolyte. In this connexion it may be noted that the rigid application of the ionic strength hypothesis to acids has on occasion led to conclusions which are quite unacceptable. For example, Harned and Hawkins (*J. Amer. Chem. Soc.*, 1928, **50**, 85) have been led to express the opinion that the ionisation constant (K_a) of chloroacetic acid must be $4{\cdot}2 \times 10^{-3}$, which is nearly three times the usually accepted value furnished by conductivity data. There can be no doubt, however, that the conductivity value ($K_0 = 1{\cdot}5 \times 10^{-3}$) is substantially a correct measure of K_a. The conductivity value is, moreover, in close agreement with the entirely independent values afforded by catalytic data relating to the action of chloroacetic acid as catalyst in the acetone–iodine and ester hydrolysis reactions.

There are many other scattered data which are difficult to reconcile with the view that the activity coefficient of an electrolyte is uniquely determined by the ionic strength of the surrounding medium. Brönsted (*J. Amer. Chem. Soc.*, 1924, **46**, 558) has, for instance, called attention to differences of the order of 60% in the values which are afforded by 0·01 molar solutions of magnesium chloride and sodium sulphate respectively.

The observations cited above lend support to the conclusion which seems to follow from the experimental results described in this paper. **These results show that the influence of salts on the ionisation of acids cannot be interpreted in terms of the interionic attraction theory unless it is assumed that the coefficient α, and therefore the mean ionic activity coefficient for acids, is much smaller than the value suggested by the Debye–Hückel theory.**

Summary.

The influence of inert salts on the ionisation of a series of acids with widely different ionisation constants has been deduced from observations on the rate of hydrolysis of ethyl acetate in sodium chloride solutions.

It is shown that experiments with hydrochloric acid afford a measure of the catalytic activity of the hydrogen ion in the salt solutions and that the observations are not measurably influenced by the interaction of chlorine ions with hydrogen ions.

The method of determining the hydrogen-ion concentration is independent of any assumption which would distinguish between the concentrations and the activities of the entities which take part in the catalysed chemical change.

The influence of the inert salt on the ionisation of the various acids may be represented by the equation $\log R_x = \log K_x/K_0 = a\sqrt{x} - bx$, where K_x and K_0 represent the ionisation constants in an x-molar salt solution and in pure water respectively. The constants a and b are approximately independent of the nature of the acid. This relation is shown to be quantitatively incompatible with the expression for R_x which is derived by application of the Debye–Hückel theory.

In contradiction to the ionic strength hypothesis it would appear that the activity coefficient of an electrolyte varies with the nature of the electrolyte and of the ionic environment.

By reference to the data for the acetone–iodine reaction it is shown that the connexion between the catalytic coefficient k_m and the ionisation constant K is closely represented by the equation $k_m = 3{\cdot}0\ k_h K^{0{\cdot}64}$.

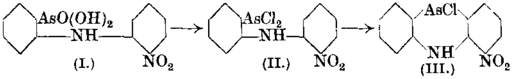
THE UNIVERSITY, LEEDS. [*Received, May 10th*, 1929.]

CLXIII.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part IX. The Synthesis of Nitromethyldiphenylamine*-6′-*arsinic Acids and their Conversion into Nitromethyl Derivatives of* 10-*Chloro*-5 : 10-*dihydrophenarsazine. Constitution of* 10-*Chloro*-5 : 10-*dihydrophenarsazine.*

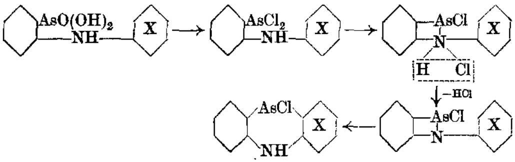
By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

FROM the experiments on the synthesis of 2-nitro-, 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines from the corresponding 4-nitro-, 3-nitro-, and 2-nitro-diphenylamine-6′-arsinic

acids (Part V, J., 1927, 2504) the following facts were noted : (*a*) The reduction of 4-nitro- and 3-nitro-diphenylamine-6′-arsinic acids in the presence of hydrochloric acid yielded nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine directly, and 2-nitrodiphenylamine-6′-arsinic acid (I) under the same conditions gave the intermediate dichloroarsine (II), which was converted into 10-chloro-4-nitro-5 : 10-dihydrophenarsazine (III) by boiling in acetic acid solution; and (*b*) the 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines are deep red, whereas the 2-nitro-compound is yellow.



Of the many substituted diphenylamine-6′-arsinic acids which have been described in this series of communications, compound (I) is unique in yielding an isolable dichloroarsine on reduction, and 1(or 3)-nitro- and 4-nitro-10-chloro-5 : 10-dihydrophenarsazines are remarkable in possessing a deep red colour, whereas all the other derivatives of the parent substance are either yellow or colourless. At that time the following scheme of formation of derivatives of 10-chloro-5 : 10-dihydrophenarsazine from substituted diphenylamine-6′-arsinic acids, in which the dichloroarsine is always an intermediate product, was suggested :



When the substituent group (X) is a nitro-group, nitrogen-arsenic ring formation would not take place so readily because of the diminished basicity of the nitrogen atom, and this would be especially marked in the case where the nitro-group is adjacent to the nitrogen atom.

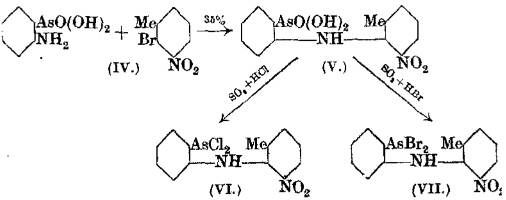
One of the objects of the present work was to study the cyclisation of diphenylamine-6′-arsinic acids in greater detail, since, if the ring-formation process follows the course suggested above, all substituted diphenylamine-6′-arsinic acids having a nitro- or other strongly electronegative group in the ortho-position to the :NH group should yield isolable dichloroarsines on reduction in the

presence of hydrochloric acid. Secondly, although deductions concerning the constitutions of substances based upon visible colour are subject to criticism, in this further work evidence has been obtained which enables us to state with some certainty the constitution of the reduction product of 3-nitrodiphenylamine-6′-arsinic acid. The particular case of the direction of ring closure of 3-methyldiphenylamine-6′-arsinic acid, which may yield 10-chloro-1(or 3)-methyl-5 : 10-dihydrophenarsazine, has already been discussed (Part VII, this vol., p. 767), and the cyclisation of 3-nitrodiphenylamine-6′-arsinic acid is a subject of the same nature. Finally, the properties of a large number of new substances which have been prepared afford some indication of the constitution of the parent substance and of its derivatives.

By studying the preparation of various *nitromethyldiphenylamine*-6′-arsinic acids and their ring closure it has been possible to investigate the above three problems. The nitromethyldiphenylamine-6′-arsinic acids were chosen partly because they were for the most part moderately easily accessible and the introduction of two different groups increases the number of possible isomerides, enabling conclusions to be drawn from a large number of cases, and partly because the nitro-group could be forced into a specified position by blocking with the methyl group one of the available *ortho*-positions to the :NH group.

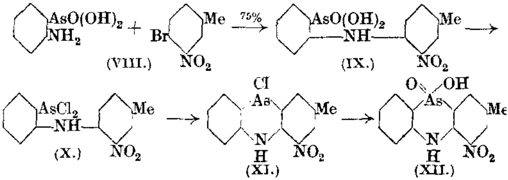
The nitromethyldiphenylamine-6′-arsinic acids were prepared on the one hand by condensing bromonitrotoluenes with *o*-aminophenylarsinic acid and, on the other hand, by condensing bromonitrobenzenes with aminotolylarsinic acids under the previously described conditions (Part V, *loc. cit.*). Twelve of the possible thirty-four acids are described in the present communication.

Using 2-*bromo*-3-*nitrotoluene* (IV), the following series of reactions was carried out, the relatively low yield of 2-nitro-6-methyldiphenylamine-6′-arsinic acid (V) being undoubtedly due to steric hindrance :



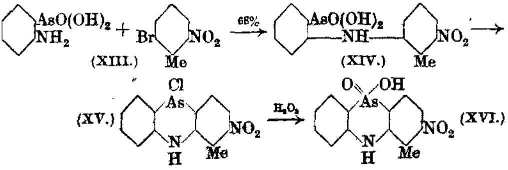
Compound (V) is highly crystalline and yellow and markedly volatile under reduced pressure at the ordinary temperature. The *dichloro*- and *dibromo-arsines* (VI and VII) cannot be converted into tricyclic compounds.

Starting with 4-bromo-3-nitrotoluene (VIII), the following series of reactions was accomplished :



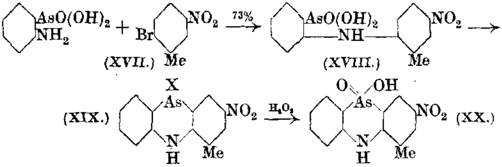
Compound (IX) again was golden-yellow and somewhat volatile under reduced pressure. On reduction, as was expected, the corresponding *dichloroarsine* (X) was formed and was obtained as an orange-yellow crystalline substance. It was distinguished from derivatives of 10-chloro-5 : 10-dihydrophenarsazine by its high solubility in the usual organic solvents and its low melting point (91—93°). On boiling with acetic acid, hydrogen chloride was evolved and *10-chloro-4-nitro-2-methyl-5 : 10-dihydrophenarsazine* (XI) was produced. This was crimson, had m. p. 187—188°, and was less soluble in organic solvents than the dichloroarsine but more soluble than those derivatives of 10-chloro-5 : 10-dihydrophenarsazine having the nitro-group in the 2-position. Reduction of (IX) in the presence of hydrobromic acid gave an oil mixed with solid material. The latter was shown to be the *bromo*-derivative corresponding to (XI) ; the former, although it could not be purified, had all the properties of the open-chain *dibromoarsine* corresponding to (X). In this case, it appears that partial ring closure takes place in the presence of hydrobromic acid.

The next series of reactions investigated was the following :



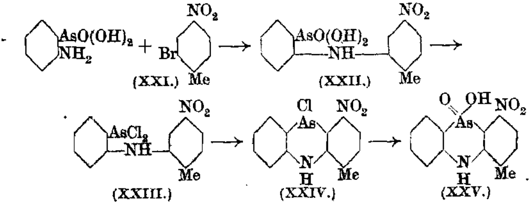
The compound (XIV) is pale yellow and yields the cyclic compound (XV) directly on reduction. In the preparation of the corresponding *bromo*-compound, the primary formation of an oil was observed, but it rapidly solidified and when crystallised from benzene (a medium which does not appear to favour cyclisation) only 10-*bromo*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* was isolated. The reduction of (XIV) to the chloro-compound (XV) is one of the cases where the nitro-group is forced into a definite position owing to the blocking effect of the methyl group.

The next series of reactions was the following :



Compound (XVIII) is pale yellow and decomposes at a high temperature. It yields compound (XIX) (X = Cl or Br) on reduction, no indication of the formation of a dichloro- (or dibromo-) arsine being observed. The sodium and potassium salts of 2-*nitro*-4-*methylphenarsazinic acid* (XX) show remarkable colour changes on dilution and addition of alkali; these colour changes appear to be characteristic of the 2-nitrophenarsazinic acids.

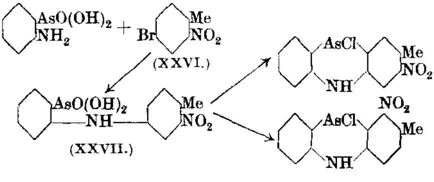
The most unexpected result in this part of the present investigation was the observation that 5-*nitro*-2-*methyldiphenylamine*-6′-*arsinic acid* (XXII), prepared as indicated, gave a *dichloroarsine* (XXIII) on reduction :



This was bright yellow and, for a dichloroarsine, had the unusually high m. p. of 173°. On boiling in acetic acid solution for 2 hours,

ring closure was effected and 10-*chloro*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XXIV) was produced. This is another case where the nitro-group is forced into a definite position because of the presence of the methyl group. The substance (XXIV) was deep red, not very soluble in the usual organic solvents, and had a high m. p. (258—260°). When compound (XXII) was reduced in the presence of hydrobromic acid, a mixture of yellow *dibromoarsine*, m. p. 164°, and deep red 10-*bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, decomp. 272°, was obtained. The *phenarsazinic acid* (XXV) obtained by oxidising compound (XXIV) underwent complex reactions when heated with alkalis, yielding amorphous, discoloured, acidic products presumably of the Mikado-brown type.

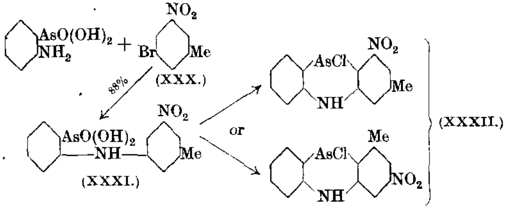
The three other bromonitrotoluenes on condensation with *o*-aminophenylarsinic acid furnished nitromethyldiphenylamine-6′-arsinic acids which could theoretically give rise to two cyclic products in each case on reduction. In only one case were two isomeric cyclic compounds isolated, namely, when 3-*nitro*-4-*methyldiphenylamine*-6′-*arsinic acid* (XXVII) was reduced in the presence of hydrochloric acid. The following was the series of reactions investigated :



(XXVI.) (XXVII.) (XXVIII.) (XXIX.)

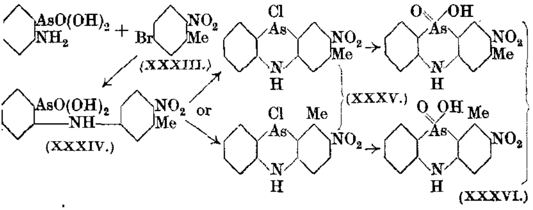
The acid (XXVII), purified through its *barium* salt, when reduced in the usual manner gave an orange-yellow precipitate, and the filtrate from this gave a red product on further treatment with sulphur dioxide. The former was only slightly soluble in benzene, and the latter crystallised in bright red needles, decomp. 225—226°. The orange-yellow material crystallised from acetic acid in orange-yellow prisms, decomp. 257—258°. Since the two substances could be crystallised side by side from benzene, it cannot be a case of dimorphism, and analysis showed that the products can only be the two substances (XXVIII) and (XXIX). The oxidation products of these two substances, the corresponding phenarsazinic acids, could not be distinguished from each other by the methods at our disposal.

The next series of reactions investigated was the following :



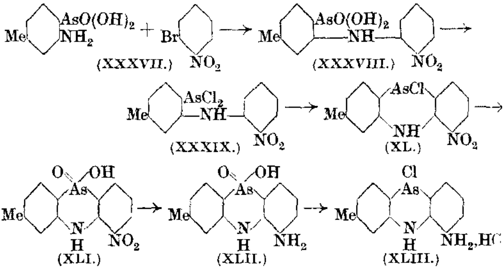
The orange-yellow product (XXXII) had m. p. 225—228° and since it was insoluble in the ordinary organic solvents the probability of its being a derivative of 10-chloro-5 : 10-dihydrophenarsazine and not a dichloroarsine was indicated. On crystallisation from butyric acid, the best solvent, it formed orange-coloured needles, decomp. 245—247°. The substance appeared to be homogeneous. The *bromo*-compound, prepared similarly, was deep red and also appeared to be homogeneous, although its melting point was somewhat indefinite.

After some difficulty *4-nitro-3-methyldiphenylamine-6′-arsinic acid* (XXXIV) from the condensation of 3-bromo-6-nitrotoluene (XXXIII) with *o*-aminophenylarsinic acid was obtained in pale yellow needles. The reduction product (XXXV) when crude had m. p. 220—228° (decomp.) and this was only raised to 236—238°



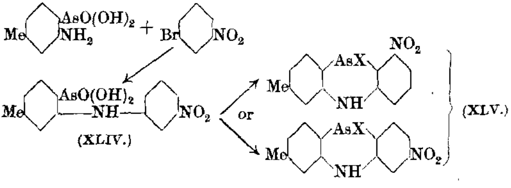
after crystallisation from acetic acid. This indicated that cyclisation had taken place along with the reduction, and the product, orange-yellow needles, appeared to be homogeneous. The corresponding phenarsazinic acid (XXXVI) obtained from this by oxidation showed the remarkable colour changes with alkalis already noted in the case of compound (XX).

Several methylnitrodiphenylamine-6′-arsinic acids in which th methyl and nitro-groups were in different rings were next studied The first of this series of reactions investigated was :



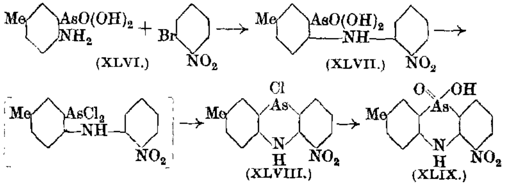
Compound (XXXVIII) is golden-yellow, and volatile under reduced pressure at the ordinary temperature; compound (XL) also is appreciably volatile under the same conditions.

The condensation products from *m*- and *p*-bromonitrobenzenes and 3-*amino*-*p*-*tolylarsinic acid* (XXXVII) were *difficult* to purify and work on that produced from *p*-bromonitrobenzene was especially restricted. The following illustrates the reactions carried out with *m*-bromonitrobenzene, the cyclic *chloro*- and *bromo*-compounds (XLV) (X = Cl or Br) being obtained as deep red substances difficult to purify.



Finally, 4-amino-*m*-tolylarsinic acid (XLVI) was condensed with *o*-bromonitrobenzene: the product, 2-*nitro*-4′-*methyldiphenylamine-6′-arsinic acid* (XLVII), had properties similar to those of the acid (XXXVIII). On reduction an uncrystallisable oil was obtained. Its ready solubility and the fact that hydrogen chloride was evolved on boiling it in acetic acid solution indicated

that it was the dichloroarsine; the product obtained on boiling with acetic acid was the cyclic compound 10-*chloro*-4-*nitro*-8-*methyl*-5 : 10-*dihydrophenarsazine* (XLVIII), which on oxidation with hydrogen peroxide gave the phenarsazinic acid (XLIX).



The following summarises the more important observations arising from the experiments :

(1) All substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the ortho-position to the :NH group, on reduction in the presence of hydrochloric acid, yield dichloroarsines (compounds I, V, IX, XXXVIII, XLVII).

(2) All substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the para-position to the :NH group, on reduction in presence of hydrochloric acid, yield the corresponding cyclic chloro-compound, *e.g.*, 4-nitrodiphenylamine-6′-arsinic acid (J., 1927, 2504) (compounds XVIII and XXXIV).

(3) With the exception of 5-nitro-2-methyldiphenylamine-6′-arsinic acid (XXII), all substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the meta-position to the :NH group, on reduction in presence of hydrochloric acid, yield the corresponding cyclic chloro-compound, *e.g.*, 3-nitrodiphenylamine-6′-arsinic acid (J., 1927, *loc. cit.*) (compounds XIV, XXVII, XXXI, and XLIV).

(4) All substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines are crimson, have lower melting points than the other nitro-10-chloro-5 : 10-dihydrophenarsazines, are generally more soluble in organic solvents, and are volatile under diminished pressure at the ordinary temperature.

(5) All substituted 10-chloro-2-nitro-5 : 10-dihydrophenarsazines are yellow, are soluble with difficulty in the usual solvents, and generally have very high melting points. The exceptionally low melting point of 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine (XXXV, 236—238°) will be discussed later.

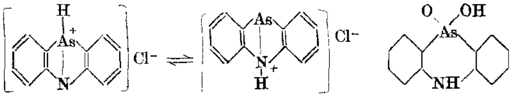
(6) One derivative of 10-chloro-5 : 10-dihydrophenarsazine, in which the nitro-group is definitely in the 3-position, *viz.*, 10-chloro-

3-nitro-4-methyl-5 : 10-dihydrophenarsazine (XV), is yellow and has m. p. 216·5°.

(7) One derivative, in which the nitro-group is definitely in the 1-position, 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine (XXIV), is deep red, has m. p. 258—260°, but is not generally so soluble in organic solvents as the 4-nitro-compounds.

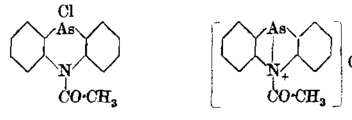
(8) The 2-nitrophenarsazinic acids give the characteristic colour changes with alkalis which have been noted above.

The following explanation of the results is suggested. All the simple derivatives of 10-chloro-5 : 10-dihydrophenarsazine in which the arsenic atom is in the tervalent condition are yellow unless the hydrogen of the :NH group has been replaced by an acyl group, in which case the compounds are practically colourless. Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) suggested that the yellow colour of 10-chloro-5 : 10-dihydrophenarsazine was due to an atomic interaction between the arsenic and nitrogen atoms which involves their possessing a quinonoid-like structure. Sufficient experimental evidence has now been provided to ascribe to this parent compound the constitution (L) or (LI), which may be in equilibrium.



(L.) (LI.) (LII.)

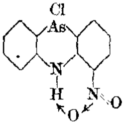
Since visible colour is absent in the case of phenarsazinic acid (LII), where a transannular N—As bond is precluded, it would appear that the yellow colour of 10-chloro-5 : 10-dihydrophenarsazine is due to the presence of the transannular structure indicated above. The colourless nature of 5-acetyl-10-chloro-5 : 10-dihydrophenarsazine (LIII) is readily explained, since the presence of a transannular bond as in (LIV) would necessitate the nitrogen atom carrying a

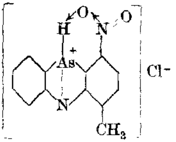
(LIII.)  (LIV.)

positive charge although it has the negative acetyl group attached to it.

The physical properties of the 4-nitro-derivatives are those usually associated with chelate compounds and since these properties are generally absent in the case of the 2-nitro-compounds it is reasonable

to assume that the chelate ring formation is a consequence of the proximity of the nitro- and :NH groups as indicated in formula (LV).

(LV.) 

 (LVI.)

The deep red colour of the 4-nitro-compounds must then be associated with the presence of the chelate ring and consequently those substances in which the presence of the chelate ring of the type above mentioned is precluded should not possess a deep red colour. This is actually the case, compound (XV) and all the 2-nitro-derivatives being yellow or orange-yellow. On the other hand, 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine (XXIV) is deep red, and this suggests a structure similar to (LV). This can readily be assigned to the substance if the transannular bond is also present, the constitution then being that indicated by (LVI). The difference between (LV) and (LVI) is that the latter is a salt whereas the former has simply co-valencies. The high melting point of (LVI) (258—260°) compared with those of the 4-nitro-derivatives of type (LV) [187—188° (XII), 201—202° (XL), 206° (XLVIII)] and its lower solubility in organic solvents are in agreement with this view.*

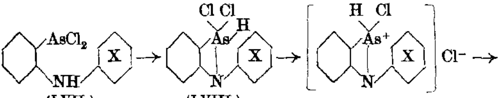
Following from this argument, provisional constitutions may be assigned to those compounds which may be 1(or 3)-nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine. The reduction product of 3-nitro-3′-methyldiphenylamine-6′-arsinic acid (XLIV) may be 10-chloro-1(or 3)-nitro-7-methyl-5 : 10-dihydrophenarsazine. It is deep red in colour and has m. p. 253—255°, indicating the 1-nitro-structure. Similarly, the deep red reduction product of 3-nitro-diphenylamine-6′-arsinic acid (J., 1927, 2504) has most probably the 1-nitro-structure. On the other hand, the reduction product of 5-nitro-3-methyldiphenylamine-6′-arsinic acid (XXXI) is orange-yellow and has m. p. 245—247°, suggesting the 3-nitro-structure.

* Through the kind co-operation of Sir Robert Robertson, Dr. J. J. Fox, and Mr. E. S. Hiscocks the absorption spectra in the visible and ultra-violet regions of the most typical of these compounds are being examined and it is hoped to describe the results in a future communication. The differences in the visible colour, however, are so marked that the authors feel justified in basing conclusions upon them. Preliminary work shows that the accurate determination of the absorption spectra of these highly complicated substances confirms the conclusions now drawn.

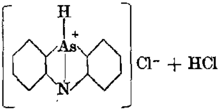
The most convincing evidence is probably that furnished by the *reduction products of 3-nitro-4-methyldiphenylamine-6′-arsinic acid* (XXVII). These must be 3-nitro-2-methyl- and 1-nitro-2-methyl-10-chloro-5 : 10-dihydrophenarsazines respectively. The more soluble, lower-melting isomeride is deep red; the less soluble, higher-melting compound is orange-yellow. To the former, the 1-nitro-structure (XXIX) is assigned, whereas the latter is presumed to be the 3-nitro-compound (XXVIII).

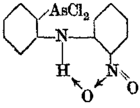
It is clear that the proximity of the methyl and nitro-groups may have some effect on the melting point, and this is especially marked in the case of the 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine (XXXV), where the nitro- and methyl groups are in the ortho-position with respect to each other. Chelate ring formation is possible, mutual saturation follows, and less residual affinity remains to bind molecule to molecule, resulting in a lower melting point (236—238°) than is usual with 2-nitro-derivatives.

Since there is the probable presence of a chelate ring in the substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines, the presence of a similar structure in the corresponding open-chain acids and dichloroarsines is also probable. This is in accord with the observations that the former are volatile under reduced pressure at the ordinary temperature and more easily soluble than the 3- and 4-nitrodiphenylamine-6′-arsinic acids, and that the dichloroarsines are low-melting solids of high solubility. In view of this a more detailed explanation of the mechanism of, and factors underlying, ring closure is now possible. In the simple general case, the dichloroarsine will be formed first; the $-AsCl_2$ group will react with the :NH group, hydrogen chloride will be eliminated, and the ring chloro-compound formed. The following mechanism seems to fit the facts better than that previously put forward (p. 1230).



(LVII.) (LVIII.)



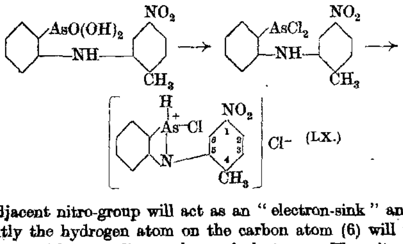


(LIX.)

The presence of any group in the dichloroarsine (LVII) which prevents or inhibits the movement of the hydrogen atom of the

:NH group will prevent or inhibit the subsequent formation of the substance represented by (LVIII) and consequently the dichloroarsine will be stable. A nitro-group in the 2-position in (LVII) would, owing to the presence of a chelate ring as in (LIX), restrict the movement of the hydrogen atom; consequently all 2-nitrodiphenylamine-6′-arsinic acids should yield stable dichloroarsines. In solution in a substance of high dielectric constant, this chelate ring would be weakened and conversion of the dichloroarsine into the ring chloro-compound would not be impeded to such an extent as before. Acetic acid, having a dielectric constant of about 9, is such a solvent and hence ring closure is effected on boiling in acetic acid solution but not in benzene.

3-Nitro- and 4-nitro-diphenylamine-6′-arsinic acids would not show this peculiarity unless some other factor played a part. The one case where a dichloroarsine was isolated although the nitro-group was not in the ortho-position to the :NH group is such an exception. The dichloroarsine isolated on reducing 5-nitro-2-methyldiphenylamine-6′-arsinic acid (XXII) was bright yellow and had m. p. 173°, which is unusually high for a dichloroarsine. The latter property suggests a salt-like structure, and the former suggests a constitution resembling the transannular bond structure postulated for 10-chloro-5 : 10-dihydrophenarsazine. The structure represented by (LX) is in agreement with these views. The positive character now acquired by the arsenic atom will be in part transmitted to the attached chlorine atom; the ease with which hydrogen chloride is eliminated will depend upon the extent to which the hydrogen atom attached to carbon atom (6)—which will be eliminated as hydrogen chloride—will be able to make up the electron deficiency associated with the chlorine atom.



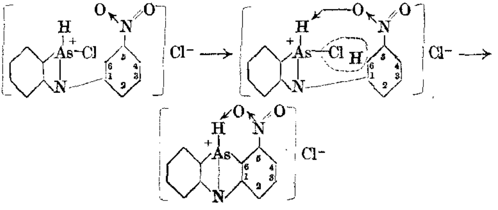
(LX.)

The adjacent nitro-group will act as an "electron-sink" and consequently the hydrogen atom on the carbon atom (6) will not be associated with its ordinary share of electrons. The nitro-group will, then, diminish the tendency for the elimination of hydrogen chloride and the dichloroarsine (LX) will possess some measure of

stability. Solution of the dichloroarsine in a substance of high dielectric constant (such as acetic acid) would diminish electrostatic forces in the molecule and the elimination of hydrogen chloride would be assisted.

We have yet to consider the course of the reactions which lead to the formation sometimes of 1-nitro- and sometimes of 3-nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine. In two cases, cyclisation appeared to yield only the 1-nitro-compound; in these cases no methyl group was present in the same ring as the nitro-group. In one case, cyclisation yielded apparently only the 3-nitro-derivative, and in another case, a mixture of the 1- and the 3-nitro-derivative was produced. In the latter cases, a methyl group was present in the same ring as the nitro-group. The factors which influence the direction of ring closure are the steric factor, the polar factor, and that due to the restricted rotation of the right-hand nucleus, due partly to the steric factor and partly to the polar factor.

Considering the cases where only the 1-nitro-compound was formed, it will be seen that the steric factor would favour the formation of the 3-nitro-derivative. Secondly, because of the proximity of the nitro-group, the hydrogen atom on carbon atom (6) would have less association with electrons than that on carbon atom (2). This also would favour the formation of the 3-nitro-derivative. But since there is evidence of the presence of a chelate ring in the 1-nitro-compounds, it is probable that this exists prior to the final ring closure. Free rotation is thus prevented and ring closure takes place on the carbon atom (6).



When a methyl group is present in the 3-position, the steric factor will still favour ring closure to give the 3-nitro-compound. The polar factor would now have the predominant effect, for the hydrogen atom on the carbon atom (2) would have a large electron surplus compared with that on carbon atom (6) because of the proximity of the electron source (the methyl group) at position (3)

and the remoteness of the " electron sink " (the nitro-group). The polar factor is now able to outweigh the combined effects of the steric factor and that due to restricted rotation, and the 3-nitro-compound results.

Finally, the intermediate case where both the 1- and the 3-nitro-compound are formed can be explained in similar fashion. The " electron source " is now at position (4), its effect is diminished at (2) and increased slightly at (6). An intermediate effect is obtained and both isomerides are produced.

This explanation of the mechanism of ring closure, while admittedly imperfect, is considered the most likely and further work in this field will probably produce more evidence in its favour.

The present work has shown that there is a greater tendency for ring closure in the case of the bromo-compounds than in the case of the chloro-compounds. This also is in keeping with the above suggestions, since one would expect that the less electronegative bromine atom would be more satisfied with a hydrogen atom not too richly associated with electrons than a chlorine atom would; hence the conversion of the bromine analogue of (LX) into the ring compound should be more facile than that of the chloro-compound and this agrees with the experimental result.

EXPERIMENTAL.

Of the ten theoretically possible bromonitrotoluenes, only seven have been described. An eighth—2-*bromo*-3-*nitrotoluene*—has now been prepared and the methods of preparation of some of those already known have been modified and improved. Improved methods of preparation of some of the intermediate compounds have also been developed.

Aceto-*o*-toluidide has the following boiling points: 176°/14 mm., 184°/21 mm., 194°/32 mm.

2-*Bromo*-3-*nitrotoluene* (IV).—A suspension of finely divided 2-amino-3-nitrotoluene (50 g.) in a mixture of hydrobromic acid (36%, 35 c.c.) and water (90 c.c.) was diazotised below 0° with a solution of sodium nitrite (23·5 g.) in water (40 c.c.). The filtered diazonium solution was run fairly rapidly with constant stirring into a solution of cuprous bromide [prepared by saturating with sulphur dioxide a mixture of copper sulphate solution (crystals 60 g., in water 200 c.c.) and potassium bromide solution (30 g., in water 70 c.c.)] in hydrobromic acid (*d* 1·49, 110 c.c.) without external cooling. After being stirred for a few minutes, the mixture was heated on the water-bath for about 30 minutes, and the 2-bromo-3-nitrotoluene isolated by steam distillation. The distillate was extracted with ether; the extract was washed with dilute sodium

hydroxide solution and with water, dried with calcium chloride and evaporated, and the residue distilled under reduced pressure. 2-*Bromo*-3-*nitrotoluene* was obtained in 67% yield as a yellow solid, m. p. 41—42°, b. p. 135—136°/8 mm. and 157°/22 mm. (Found : Br, 36·7. $C_7H_6O_2NBr$ requires Br, 37·0%). It is readily soluble in alcohol and almost insoluble in water. If the molten substance is allowed to cool slowly, it forms long thick six-sided prisms.

2-Bromo-5-nitrotoluene (XVII) was prepared in a similar way (66% yield) from 2-amino-5-nitrotoluene (30 g.) in a mixture of hydrochloric acid (40 c.c.) and water (55 c.c.), the quantities of the other materials being proportionate. Instead of being isolated by steam distillation, the product, after being heated on the water-bath, was cooled, diluted, and filtered, and the 2-bromo-5-nitrotoluene crystallised from a little alcohol (charcoal); m. p. 75—76° (compare Nevile and Winther, *Ber.*, 1880, **13**, 969).

The following experimental details for the preparation of 2-amino-4-nitrotoluene supplement those supplied by Anschütz and Heusler (*Ber.*, 1886, **19**, 2161). A hot solution of 2 : 4-dinitrotoluene (91 g.) in alcohol (95%, 1 litre) was rapidly cooled in order to obtain the compound in a fine state of division. Dry hydrogen chloride was passed into a mixture of stannous chloride (crystals, 339 g.) and alcohol (95%, 680 c.c.) until a clear solution resulted. The latter solution was then added in small portions with cooling and shaking to the suspension of the dinitro-compound. A clear yellow solution resulted. After 30 minutes, the alcohol was distilled off on the water-bath, water added to the residue and then sodium hydroxide until the bulk of the tin precipitate had redissolved. The liquid was extracted twice with ether; the ethereal extract was washed twice with water, dried with calcium chloride, and evaporated to dryness. A tarry mass remained which partly solidified. This was allowed to drain on porous porcelain and the solid 2-amino-4-nitrotoluene remaining was pure after one crystallisation from benzene-ligroin (b. p. 60—80°). The yield was poor—20 g.; m. p. 107°.

2-Bromo-4-nitrotoluene (XXI) was prepared in 86% yield from 2-amino-4-nitrotoluene exactly as described for 2-bromo-3-nitrotoluene. After removal of the ether, it was obtained pure and had m. p. 76° (compare Scheufelin, *Annalen*, 1885, **231**, 171; Wallach, *ibid.*, 1886, **235**, 248; Nevile and Winther, *Ber.*, 1881, **14**, 418).

2 : 6-Dinitrotoluene was obtained in poor yield by deamination of 2 : 6-dinitro-4-aminotoluene (compare Hollemann and Böeseken, *Rec. trav. chim.*, 1897, **16**, 427).

2-Amino-6-nitrotoluene (compare Cunerth, *Annalen*, 1874, **172**,

223) was obtained in 49% yield from 2 : 6-dinitrotoluene by the following method. The dinitro-compound (43 g.) was dissolved in hot alcohol (95%, 107 c.c.) and obtained in a finely divided state by rapid cooling. Ammonium sulphide (about 86 c.c.), prepared by saturating ammonia (20%) with hydrogen sulphide, was added in small portions to this suspension with thorough shaking but without cooling. The mixture became hot, a deep red solution resulted, and crystalline material began to separate. After 1 hour, the product was evaporated to dryness, and the residue extracted with boiling hydrochloric acid (*d* 1·075) until the extracts no longer gave a precipitate on basification with sodium hydroxide. The whole extract was basified with sodium hydroxide and cooled, and the precipitated nitro-amine crystallised from benzene–ligroin (b. p. 60—80°).

2-Bromo-6-nitrotoluene (XIII) (Noelting, *Ber.*, 1904, **37**, 1021) was obtained in 93% yield from the preceding compound by the method described for 2-bromo-3-nitrotoluene; b. p. 143°/22 mm., m. p. 42°.

3-Amino-6-nitrotoluene was prepared by nitrating *m*-toluidine according to the method of Noelting and Stoecklin (*Ber.*, 1891, **24**, 564). 3-Bromo-6-nitrotoluene (XXXIII) was prepared in 81% yield from the corresponding amino-compound by the method used for the preparation of 2-bromo-3-nitrotoluene; m. p. 56°. (Compare Wroblewski, *Annalen*, 1873, **168**, 170; Grete, *ibid.*, 1875, **177**, 246, who prepared this substance by nitrating *m*-bromotoluene. The constitution of the nitration product is thus established.)

3-Bromo-2-amino-5-nitrotoluene (compare Nevile and Winther, *Ber.*, 1880, **13**, 964) was prepared by adding bromine (23·3 c.c.) drop by drop to a solution of 2-amino-5-nitrotoluene (70 g.) in acetic acid (700 c.c.). (It was necessary to warm the acetic acid to dissolve the nitro-amine, but by rapid cooling a supersaturated solution was obtained to which the bromine was added.) A pale yellow crystalline mass was precipitated; on pouring the product into water, a bulky yellow precipitate was obtained and this was filtered off and extracted with water. The dry substance (99 g.) had m. p. 176° and was sufficiently pure for the following preparation.

3-Bromo-5-nitrotoluene (XXX) (Nevile and Winther, *loc. cit.*, p. 969).—Finely divided 3-bromo-2-amino-5-nitrotoluene (65 g.) was mixed with alcohol (300 c.c.), and sulphuric acid (72 c.c.) slowly added with constant stirring. The mixture was treated slowly at the ordinary temperature with a solution of sodium nitrite (20·8 g.) in water (45 c.c.), and the product heated on the water-bath until the evolution of nitrogen and acetaldehyde was completed. The resulting mixture was submitted to steam dis-

tillation. The distillate was extracted with ether, and the ethereal extract worked up in the usual manner. On removal of the ether, the 3-bromo-5-nitrotoluene was obtained pure (m. p. 83°) without crystallisation. The average yield in four experiments was 40%.

3-Bromo-5-aminotoluene was prepared by adding a hot solution of 3-bromo-5-nitrotoluene (64·3 g.) in alcohol (514 c.c.) in small quantities at a time to a solution of stannous chloride (crystals, 258 g.) in hydrochloric acid (386 c.c.) previously heated to 60° in a 3-litre flask fitted with a reflux condenser; a vigorous reaction took place. After heating for 30 minutes on the water-bath, some of the alcohol was evaporated and the residue treated with sodium hydroxide until the tin precipitate just dissolved. The 3-bromo-5-aminotoluene was isolated by steam distillation and extraction with ether in the ordinary way. It was distilled twice under reduced pressure. The pure, colourless material was obtained in 84% yield and had b. p. 151°/23·5 mm., 157·5°/28 mm., m. p. 37—38°. Attempts to nitrate its acetyl derivative were unsuccessful or led to dinitro-compounds. Further attempts to prepare 3-bromo-2-nitrotoluene will be described later.

4-Bromo-2-nitrotoluene (XXVI) was prepared from 4-amino-2-nitrotoluene, and 4-bromo-3-nitrotoluene (VIII) from 4-amino-3-nitrotoluene, as described for 2-bromo-3-nitrotoluene.

In the following description of new organic arsenicals, attention has been paid to a complete description of the salts of acids where these are characteristic. The melting points of many of the acids lie close together and the salts described may serve for purpose of identification.

2-Nitro-3'-methyldiphenylamine-6'-arsinic Acid (XXXVIII).—A mixture of 3-amino-*p*-tolylarsinic acid (23·1 g.), *o*-bromonitrobenzene (20·2 g.), anhydrous potassium carbonate (17·3 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled for 5 hours. After removal of the amyl alcohol by steam distillation, the hot aqueous solution was filtered, cooled, and carefully acidified with concentrated hydrochloric acid. The precipitated acid (23·1 g., 66%), recrystallised from dilute acetic acid (charcoal), was obtained in clusters of well-defined, golden-yellow, prismatic needles, m. p. 215—217° (decomp.) after slight softening (Found: As, 21·6. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%).

This nitro-acid is somewhat volatile, as is also 10-chloro-4-nitro-7-methyl-5 : 10-dihydrophenarsazine (XL). When either of these pure substances is left over potassium hydroxide under reduced pressure, a deep red crust is rapidly formed on the surface of the drying agent. The amphoteric nature of the above acid is shown by its solubility in a mixture of alcohol and hydrochloric acid and

in aqueous alkali. It is scarcely soluble in cold or hot alcohol and is only moderately easily soluble in acetone. The alkali salts give deep red solutions; the magnesium salt is formed only on boiling with magnesia mixture.

2-Nitro-3'-methyldiphenylamine-6'-dichloroarsine (XXXIX).—A boiling solution of the preceding substance (1·0 g.) in a mixture of alcohol (6·0 c.c.) and hydrochloric acid (8·0 c.c.) containing a trace of iodine was reduced hy passing a rapid stream of sulphur dioxide for 5 minutes. A dark-coloured oil separated which became semi-solid on cooling; it was extracted with benzene (about 100 c.c.), and the benzene solution dried over calcium chloride and concentrated to about 15 c.c. on the water-bath. On cooling, the *dichloroarsine* was slowly deposited in bright yellow, rhomb-shaped plates. After recrystallisation from benzene it bad m. p. 129·5—130° (Found: Cl, 19·3. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%). It is readily soluble in hot benzene, moderately easily soluble in acetic acid, and almost insoluble in ligroin.

10-Chloro-4-nitro-7-methyl-5 : 10-dihydrophenarsazine (XL).—2-Nitro-3'-methyldiphenylamine-6'-arsinic acid (10·75 g.) was reduced as just described, the crude dichloroarsine remaining after evaporation of the benzene being boiled in acetic acid solution (140 c.c.) for 1½ hours. Hydrogen chloride was freely evolved and red crystalline material, ultimately filling the liquid, gradually separated. After cooling, the precipitate was filtered off and recrystallised from acetic acid (1 g. in 25 c.c. when boiling). The *compound* (7·4 g., 72% yield) crystallised in sheaves of deep red, doubly refracting needles, m. p. 201—202° (without decomp. but with previous slight softening) (Found: Cl, 10·3. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is readily soluble in hot acetone or benzene, slightly soluble in these cold solvents, and insoluble in ligroin (b. p. 80—100°). When an aqueous solution of chloramine-T was warmed with an acetone solution of the compound, a bright yellow acid was precipitated, but the method was not suitable for the preparation of the nitrophenarsazinic acid.

4-Nitro-7-methylphenarsazinic Acid (XLI).—A suspension of finely divided 10-chloro-4-nitro-7-methyl-5:10-dihydrophenarsazine (5·5 g.) in acetic acid (55 c.c.) was mixed with hydrogen peroxide (20 vols., 36 c.c.) and gently heated to boiling. The deep red colour of the chloro-compound was rapidly replaced by the yellow-orange colour of the nitrophenarsazinic acid. Oxidation was completed by heating for 15 minutes on the water-bath. After cooling, water (110 c.c.) was added and the solid material filtered off, well washed with water, and dissolved in a hot dilute aqueous solution of sodium hydroxide. The hot liquid was filtered from non-acidic substances,

and the filtrate cooled; the orange-coloured sodium salt then separated in rhomb-shaped plates. This was dissolved in hot water, the solution acidified with hydrochloric acid, and the precipitated *nitro-acid* (4·0 g.) filtered off, well washed with water, dried at 140°, and recrystallised from dilute acetic acid, giving yellow needles, m. p. 300—303° (decomp.) (Found: As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%).

This nitro-acid is not very soluble in cold aqueous alkaline solutions, but dissolves in hot dilute aqueous sodium hydroxide to a deep red solution. If this solution is treated with an excess of a strong aqueous solution of sodium hydroxide, a deep reddish-brown solution is produced, which, however, deposits the orange-coloured sodium salt on cooling. The acid dissolves in a mixture of alcohol and hydrochloric acid, is soluble in hot glacial acetic acid, slightly soluble in alcohol and acetone, and insoluble in water.

4-*Amino*-7-*methylphenarsazinic Acid* (XLII).—A hot solution of the preceding nitro-acid (3·2 g.) in dilute aqueous sodium hydroxide (0·5 g. in 60 c.c.) was added to a suspension of ferrous hydroxide prepared by mixing a solution of ferrous sulphate (crystals, 21 g.) in water (63 c.c.) with aqueous sodium hydroxide (25%, 20 c.c.) contained in a wide-mouth flask, more water (15 c.c.) being used to wash in the sodium salt of the acid. The suspension was shaken for 10 minutes and filtered. The colourless filtrate rapidly acquired an amethyst colour due to atmospheric oxidation. The residue on the filter was thoroughly washed with warm water, and the filtrate mixed with the main volume of liquid. The filtrate was cooled and carefully acidified with dilute hydrochloric acid, a slightly discoloured and somewhat gelatinous *acid* being precipitated. This was filtered off, well washed with water, and recrystallised from dilute acetic acid, short colourless needles being obtained, which remained unmelted at 310° (Found: As, 24·5. $C_{13}H_{13}O_2N_2As$ requires As, 24·7%). The acid is somewhat soluble in concentrated hydrochloric acid, easily soluble in acetic acid, and insoluble in ethyl alcohol and in water. The sodium salt is precipitated as colourless needles when a strong aqueous solution of sodium hydroxide is added to a warm aqueous solution of the sodium salt and the mixture allowed to cool. The acid is readily soluble in a mixture of alcohol and hydrochloric acid.

10-*Chloro*-4-*amino*-7-*methyl*-5 : 10-*dihydrophenarsazine Hydrochloride* (XLIII).—The preceding compound (1·0 g.), dissolved in a hot mixture of alcohol (3·0 c.c.) and hydrochloric acid (3 c.c.) containing a trace of iodine, was reduced with sulphur dioxide. A greyish-yellow crystalline solid was precipitated together with some tarry matter. After cooling, the product was filtered off, dissolved in a

hot mixture of equal volumes of ethyl alcohol and hydrochloric acid, and boiled with decolorising charcoal. To the filtrate, concentrated hydrochloric acid was added until crystalline material began to separate. 10-*Chloro*-4-*amino*-7-*methyl*-5 : 10-*dihydrophenarsazine hydrochloride* crystallises in clusters of greyish-yellow needles, m. p. 216—220° (decomp.) (Found : Cl, 20·9. $C_{13}H_{12}N_2ClAs,HCl$ requires Cl, 20·7%). It is slightly soluble in cold alcohol and readily soluble in the hot solvent.

3-*Nitro*-3′-*methyldiphenylamine*-6′-*arsinic Acid* (XLIV).—The condensation of 3-amino-*p*-tolylarsinic acid (23·1 g.) with *m*-bromonitrobenzene (20·2 g.) in boiling amyl alcohol (100 c.c.) in the presence of anhydrous potassium carbonate (17·3 g.) and a trace of copper powder gave a 73% yield of crude 3-*nitro*-3′-*methyldiphenylamine*-6′-*arsinic acid*. It was recrystallised three times from glacial acetic acid and obtained in long yellow needles, m. p. 191—192° (Found : As, 21·6. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is very soluble in hot glacial acetic acid but only slightly soluble in the cold; it is soluble in a mixture of alcohol and concentrated hydrochloric acid.

10-*Chloro*-1(or 3)-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine* (XLV).—The preceding substance (15·0 g.), dissolved in a boiling mixture of alcohol (90 c.c.) and hydrochloric acid (120 c.c.) containing a trace of iodine, was reduced in the usual manner with sulphur dioxide. The precipitated *chloro*-compound after drying was recrystallised with difficulty from nitrobenzene and thoroughly washed with benzene (Found : Cl, 10·9. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It forms deep red, small plates, m. p. 253—255° (decomp.) after slight shrinking and darkening; it is almost insoluble in benzene, acetic acid, formic acid, alcohol, and acetone, slightly soluble in chloroform, and somewhat readily soluble in *o*-dichlorobenzene and nitrobenzene.

10-*Bromo*-1(or 3)-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of 3-nitro-3′-methyldiphenylamine-6′-arsinic acid (3 g.) in alcohol (18 c.c.) and hydrobromic acid (35%, 24 c.c.) containing a trace of iodine, on reduction, yielded a deep red product, which was recrystallised with difficulty from *o*-dichlorobenzene and obtained in small, deep red plates, decomp. 248—250° after previous softening (Found : Br, 21·4. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). Its solubility is similar to that of the corresponding chloro-compound; it is also soluble in *s*-tetrachloroethane.

4-*Nitro*-3′-*methyldiphenylamine*-6′-*arsinic Acid*.—A mixture of 3-amino-*p*-tolylarsinic acid (23·1 g.), *p*-bromonitrobenzene (20·2 g.), anhydrous potassium carbonate (17·3 g.), amyl alcohol (100 c.c.), and a trace of copper powder was boiled for 5 hours. The product (89% yield), worked up as described for similar condensations,

crystallised with extreme difficulty from glacial acetic acid in minute yellow prisms, m. p. 276° (vigorous decomp.) (Found: As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%).

4-Amino-*m*-tolylarsinic acid (XLVI) was obtained in poor yield by the Béchamp reaction on *p*-toluidine (Benda, *Ber.*, 1909, **42**, 3621).

2-*Nitro*-4′-*methyldiphenylamine*-6′-*arsinic Acid* (XLVII).—A 65% yield of this compound (crude) was obtained on boiling a mixture of 4-amino-*m*-tolylarsinic acid (13·45 g.), *o*-bromonitrobenzene (11·75 g.), anhydrous potassium carbonate (10·1 g.), amyl alcohol (58 c.c.), and a trace of copper powder for 5 hours and working up the product as in similar condensations. It was readily purified by crystallisation from dilute acetic acid (about 50%) and was obtained in deep bronze-yellow, prismatic needles somewhat soluble in acetic acid. It was somewhat volatile and on standing over potassium hydroxide under reduced pressure a deep red incrustation of the potassium salt formed on the surface of the drying agent. It had m. p. 226—227° and decomposed at 234° (Found: As, 20·85. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The acid is slightly soluble in acetone. Apart from the alkali salts, which give deep red solutions, the salts are not characteristic.

Reduction of 2-*Nitro*-4′-*methyldiphenylamine*-6′-*arsinic Acid.*—A boiling solution of the preceding acid (5·25 g.) in a mixture of alcohol (30 c.c.) and hydrochloric acid (30 c.c.) containing a trace of iodine was treated with sulphur dioxide. A deeply coloured oil was precipitated. The cold supernatant liquid was decanted and the residue dissolved in benzene. The benzene solution was dried with calcium chloride and evaporated to dryness. The oily residue was taken up in benzene and cautiously treated with ligroin (b. p. 60—80°) in order to precipitate amorphous matter. Further addition of ligroin to the filtered liquid gave an oil which could not be induced to solidify. Its ready solubility in the usual organic solvents indicated that it was the dichloroarsine in an impure form. When the oil was boiled with acetic acid (30 c.c.), hydrogen chloride was evolved and at the end of 1 hour it was necessary to add more acetic acid (15 c.c.) because of the red crystalline material which had separated filling the liquid. Boiling was continued for 1 hour. 10-*Chloro*-4-*nitro*-8-*methyl*-5:10-*dihydrophenarsazine* (XLVIII) formed minute prismatic needles, m. p. 206°. It was recrystallised from acetic acid (Found: Cl, 10·6. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It was distinctly soluble in benzene, insoluble in ligroin (b. p. 60—80°), soluble in acetone, and somewhat readily volatile under reduced pressure at the ordinary temperature.

4-*Nitro*-8-*methylphenarsazinic Acid* (XLIX).—The preceding

compound (2·25 g.), suspended in cold acetic acid (23 c.c.), was treated with hydrogen peroxide (11 c.c.), and the mixture gently warmed on the water-bath. Oxidation was readily effected, the colour changing from crimson to orange-yellow. After 15 minutes, water (50 c.c.) was added, and the cold liquid filtered from the acid, which was washed with water, dissolved in cold dilute sodium hydroxide solution, and the filtered liquid acidified. The precipitated *acid* crystallised with difficulty from slightly diluted acetic acid in small, orange-yellow needles, decomp. 297—300° (Found: As, 22·45. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). It is insoluble in alcohol or acetone but dissolves in a mixture of alcohol and hydrochloric acid. The salts are very characteristic. The sodium salt (*aci*-salt of the ψ-nitro-acid?) forms bronze-yellow, hair-like needles when concentrated aqueous sodium hydroxide is added to a solution of the sodium salt. The ammonium salt is deposited from solution in hot concentrated aqueous ammonia, on cooling, in thin, deep red needles; when its aqueous solution is boiled, ammonia is evolved and the acid is precipitated. The barium salt is precipitated in clusters of reddish-yellow needles from dilute solutions; the calcium salt is slowly precipitated from dilute solutions in clusters of orange-yellow needles; the magnesium salt, obtained only on boiling the ammonium salt with magnesia mixture, forms glistening, orange-coloured, rhomb-shaped plates. The salts of the heavy metals are amorphous.

3-Nitro-2-methyldiphenylamine-6′-arsinic Acid (XIV).—A mixture of 2-bromo-6-nitrotoluene (XIII) (18·3 g.), *o*-aminophenylarsinic acid (18·3 g.), potassium carbonate (14·7 g.), amyl alcohol (85 c.c.), and a trace of copper powder, on boiling for 5 hours, gave a 68% yield of crude *3-nitro-2-methyldiphenylamine-6′-arsinic acid*. After two crystallisations from dilute acetic acid (charcoal), it was obtained in very pale yellow, glistening plates, m. p. 223—224° (decomp.) after slight softening (Found: As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The acid is readily soluble in hot alcohol. The sodium salt, precipitated on addition of 25% aqueous sodium hydroxide to a strong aqueous solution, forms pale yellow, glistening needles; the ammonium salt separates from its solution in hot concentrated aqueous ammonia, on cooling, in yellow needles. The barium salt is obtained, on cooling a hot solution containing a little ammonia, in pale, truncated, flat prisms soluble in hot water. The calcium salt, similarly prepared, crystallises in clusters of pale yellow needles.

10-Chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine (XV).—The preceding acid (8 g.), dissolved in a mixture of alcohol (45 c.c.) and hydrochloric acid (30 c.c.) containing a trace of iodine, on reduction with sulphur dioxide, gave a yellow product, m. p. 214—215°

When recrystallised from benzene, in which it was somewhat soluble, it formed thick yellow prisms, m. p. 216·5° (Found : Cl, 10·85. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is somewhat more soluble in the usual organic solvents than might have been anticipated.

10-*Bromo*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* was obtained in a similar way by reducing the arsinic acid (2·2 g.) in solution in a mixture of alcohol (12 c.c.) and hydrobromic acid (36%, 12 c.c.). The oil which was first precipitated quickly solidified and then crystallised from benzene in orange-yellow prisms, m. p. 216·5° (Found : Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%).

3-*Nitro*-4-*methylphenarsazinic Acid* (XVI).—It was necessary to heat a mixture of the chloro-compound (XV) (1·2 g.), acetic acid (12 c.c.), and hydrogen peroxide (20 vols., 6 c.c.) for 1½ hours on the water-bath to effect complete oxidation. Water (20 c.c.) was added, the precipitated acid was dissolved in warm dilute sodium hydroxide solution to separate it from non-acidic substances, the filtered liquid treated with decolorising charcoal, and concentrated sodium hydroxide solution added to the hot filtrate. On cooling, the sodium salt was precipitated in orange-yellow, thin needles. The *acid*, which was precipitated in good yield in a gelatinous form on acidification of the sodium salt, crystallised from a mixture of acetic acid and dilute hydrochloric acid in clusters of pale yellow needles. It remained unmelted at 306° (Found: As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). A solution of the sodium salt is pale orange-yellow.

4-*Nitro*-2-*methyldiphenylamine*-6′-*arsinic Acid* (XVIII).—2-Bromo-5-nitrotoluene (XVII) (25·2 g.), *o*-aminophenylarsinic acid (25·2 g.), potassium carbonate (20·2 g.), amyl alcohol (117 c.c.), and a trace of copper powder, boiled for 5 hours, gave a 73% yield of the crude condensation product. The only satisfactory method of purification was to dissolve the crude material in a boiling mixture of alcohol and concentrated hydrochloric acid and add an excess of warm water to the filtered solution. The *acid* was thus obtained in thin, pale yellow needles, decomposing vigorously at 277° (Found : As, 21·4. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water, alcohol, and acetic acid; it dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which rapidly changes to bluish-green and then, on addition of nitric acid, to olive-green and finally to orange. The salts of this acid are particularly well defined. The sodium salt is precipitated from concentrated solutions by the addition of concentrated sodium hydroxide solution in golden-yellow flat needles which dissolve in cold water, giving an orange-red solution. Addition of concentrated aqueous sodium hydroxide to this solution does not produce a purple colour (compare

2-nitro-4-methylphenarsazinic acid, below). The ammonium salt (precipitated only when 0·880 ammonia solution is used) forms orange-yellow needles which yield a deep red aqueous solution. The barium salt, prepared only in the presence of a slight excess of ammonia, forms thick yellow plates when crystallised from hot water, in which it is only slightly soluble. The calcium salt, prepared in a similar manner, forms orange-yellow plates insoluble in cold and in hot water. The magnesium salt is an orange amorphous precipitate produced when the acid is boiled with magnesia mixture. The mercurous and mercuric salts, the former soluble in ammonia, crystallise in tufts of yellow needles; the silver and lead salts are flocculent yellow precipitates, the former soluble in ammonia.

10-*Chloro-2-nitro-4-methyl-5* : 10-*dihydrophenarsazine* (XIX).—The preceding acid (10 g.) was reduced by saturating with sulphur dioxide a boiling solution in alcohol (160 c.c.) and hydrochloric acid (50 c.c.) containing a trace of iodine. The yellow precipitate was washed with alcohol and, after drying at 110°, recrystallised from *o*-dichlorobenzene, giving deep yellow needles, m. p. 303—305° (decomp.) (Found : Cl, 10·85. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is insoluble in benzene, acetic acid, alcohol, and ether, but slightly soluble in acetone. The same substance is produced when 2-nitro-4-methylphenarsazinic acid (see below) is reduced with sulphur dioxide under similar conditions to the above.

10-*Bromo-2-nitro-4-methyl-5* : 10-*dihydrophenarsazine* was obtained by reducing 4-nitro-2-methyldiphenylamine-6′-arsinic acid with sulphur dioxide in the presence of hydrobromic acid under the usual conditions. The product was finally recrystallised from *o*-dichlorobenzene and obtained in orange-yellow plates with a metallic sheen; m. p. 301—302° (decomp.) (Found: Br, 21·4. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). It is insoluble in benzene and ether and slightly soluble in alcohol, acetone, and acetic acid (see below).

2-*Nitro-4-methylphenarsazinic Acid* (XX).—Either of the two preceding compounds (3·85 g.) was boiled with acetic acid (50 c.c.); most of it dissolved. The liquid was cooled rapidly to obtain fine crystals, and hydrogen peroxide (20 vols., 25 c.c.) added. When the mixture was gently warmed and finally boiled for 5 minutes, a pale yellow solid separated; water was added after the mixture had cooled. The acid was dissolved in dilute sodium hydroxide solution, heated to boiling, and decolorised with charcoal, and the filtrate acidified with dilute hydrochloric acid. The *phenarsazinic acid* was precipitated as a pale yellow, gelatinous mass which, recrystallised from much glacial acetic acid, formed clusters of pale yellow needles, unmelted at 306° (Found : As, 22·5. $C_{13}H_{11}O_4N_2As$

requires As, 22·4%). The *ammonium* salt is precipitated in fine yellow needles by the addition of an excess of concentrated aqueous ammonia to a solution of the acid in dilute ammonia solution. On boiling a solution of the ammonium salt, ammonia is evolved and the acid is precipitated. The barium salt forms clusters of pale yellow needles insoluble in cold and in hot water. The calcium salt forms short orange-yellow prisms. The silver salt is an amorphous yellow precipitate soluble in ammonia solution; the magnesium salt, formed only on boiling, crystallises in thin yellow prisms. The mercurous and mercuric salts are pale yellow amorphous precipitates; the lead salt is similar but deep yellow. The potassium salt is precipitated from solutions in hot 25% potassium hydroxide solution on cooling, in thin golden-yellow prisms. These dissolve in water to an orange-red solution (concentrated) or pale yellow solution (dilute). Addition of 25% potassium hydroxide solution to either solution causes it to become deep purple (formation of the dipotassium salt of the ψ-acid?); on dilution, this solution becomes pale yellow, and will then again go through the same changes. The sodium salt crystallises in tufts of orange-yellow needles and its solutions behave similarly.

5-Nitro-2-methyldiphenylamine-6′-arsinic Acid (XXII).—A mixture of 2-bromo-4-nitrotoluene (XXI) (22·4 g.), *o*-aminophenylarsinic acid (22·4 g.), potassium carbonate (18 g.), amyl alcohol (104 c.c.), and a trace of copper powder was submitted to the usual treatment. The crude product was recrystallised from 50% acetic acid and obtained in 56% yield in clusters of light yellow needles, m. p. 224—226° (slight decomp.) (Found: As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The *acid* is insoluble in water, slightly soluble in cold alcohol, and somewhat readily soluble in hot alcohol. It dissolves readily in a mixture of alcohol and concentrated hydrochloric acid. The alkali salts dissolve readily in water, forming deep red solutions. The barium salt crystallises in yellow plates and the calcium salt in bright yellow needles. The lead, silver and mercurous salts are yellow gelatinous precipitates, the mercuric salt crystallises in thin yellow needles, and the magnesium salt, formed only on boiling the acid with magnesia mixture, separates in tufts of colourless needles.

5-Nitro-2-methyldiphenylamine-6′-dichloroarsine (XXIII).—A boiling solution of the preceding acid (10 g.) in a mixture of alcohol (60 c.c.) and hydrochloric acid (40 c.c.) containing a trace of iodine was reduced with sulphur dioxide. After cooling, the precipitated orange-yellow crystalline solid was separated and recrystallised from benzene and obtained in bright yellow, rhomb-shaped plates, m. p. 173° (Found: Cl, 18·5. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%).

10-*Chloro*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (XXIV).—The crude reduction product from compound (XXII) (10 g.) was added to acetic acid (40 c.c.), and the mixture boiled for 2 hours. The acetic acid solution was evaporated to one-third of its volume, and, on cooling, the product separated in thick, deep red prisms which, after recrystallisation from glacial acetic acid, had m. p. 258—260° (Found : Cl, 10·9. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). The compound is slightly soluble in hot acetic acid, sparingly soluble in acetone, alcohol, and benzene, and insoluble in ligroin, but readily soluble in boiling *o*-dichlorobenzene.

5-*Nitro*-2-*methyldiphenylamine*-6′-*dibromoarsine* and 10-*Bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of compound (XXII) (4·7 g.) in alcohol (60 c.c.) and hydrobromic acid (*d* 1·324, 60 c.c.) containing a trace of iodine was reduced with sulphur dioxide. The crystalline reduction product appeared to be a mixture of yellow and orange substances. After filtration and drying on porous porcelain, it was extracted twice with boiling benzene. The insoluble deep red substance was recrystallised from *o*-dichlorobenzene and obtained in stout, deep red prisms, decomposing vigorously at 272°. The benzene extract was evaporated to dryness and the residue recrystallised from benzene (charcoal). The yellow flat plates obtained had m. p. 164°. The substance became deep red at its melting point, partly solidified as the temperature was raised, and decomposed vigorously at 230°.

The deep red product was only slightly soluble in the usual solvents and proved to be 10-*bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (Found : Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). The yellow substance was readily soluble in acetone, hot benzene, and hot glacial acetic acid; it proved to be 5-*nitro*-2-*methyldiphenylamine*-6′-*dibromoarsine* (Found : Br, 34·2. $C_{13}H_{11}O_2N_2Br_2As$ requires Br, 34·6%).

1-*Nitro*-4-*methylphenarsazinic Acid* (XXV).—Compound (XXIV) (0·75 g.), mixed with acetic acid (7·5 c.c.) and hydrogen peroxide (20 vols., 3·7 c.c.), was slowly oxidised by heating on the water-bath for 30 minutes. The acid precipitated by the addition of water was dissolved in warm dilute aqueous sodium hydroxide (charcoal), and the filtered solution immediately acidified. The orange-yellow *acid* obtained could not be recrystallised directly; it darkened at about 295° but remained unmelted at 305° (Found : As, 22·1. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). On boiling with moderately concentrated sodium hydroxide solution for a short time, a brown amorphous acid was precipitated. This presumably was a mixture of dinitroso-, azoxy-, and azo-stilbenearsinic acid derivatives, analogous to that obtained when a simple arsinic acid

having a methyl group in the para-position to a nitro-group is treated with hot concentrated sodium hydroxide solution (compare Benda and Schultz, *Ber.*, 1886, **19**, 3234).

2-*Nitro*-6-*methyldiphenylamine*-6′-*arsinic Acid* (V).—A mixture of *o*-aminophenylarsinic acid (12·55 g.), 2-bromo-3-nitrotoluene (12·55 g.), potassium carbonate (10·1 g.), amyl alcohol (58 c.c.), and a trace of copper powder was boiled for 5 hours. The crude product (7·15 g., 35%) was obtained pure after one recrystallisation from dilute acetic acid (charcoal). The *compound* crystallises in golden-yellow plates, m. p. 195—197° (Found: As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is readily soluble in boiling glacial acetic acid, but not very soluble in the cold solvent. Dilute acetic acid is the best medium for recrystallisation. The arsinic acid is very sparingly soluble in alcohol and in water, but dissolves readily in a mixture of alcohol and concentrated hydrochloric acid. It is remarkably volatile, especially under reduced pressure. The ammonium *salt* is a yellow microcrystalline powder insoluble in excess of ammonia solution; the sodium salt is precipitated in yellow needles from a solution in concentrated aqueous sodium hydroxide; the barium salt, somewhat soluble in hot water, crystallises in orange-yellow plates and is the most characteristic salt of the acid.

2-*Nitro*-6-*methyldiphenylamine*-6′-*dichloroarsine* (VI).—A boiling solution of the preceding compound (2 g.) in alcohol (15 c.c.) and hydrochloric acid (15 c.c.) containing a little iodine, on reduction with sulphur dioxide, gave a deeply coloured, heavy oil, which was separated by decantation and dissolved in benzene; the benzene solution was washed with concentrated hydrochloric acid and dried with calcium chloride, and the benzene evaporated. The residue was again dissolved in benzene, and the amorphous material separated by the careful addition of ligroin. The filtrate was again evaporated to dryness, and the somewhat resinous residue recrystallised from a small quantity of glacial acetic acid. The *dichloroarsine* was thus obtained in small, orange-yellow prisms, m. p. 104—105° (Found: Cl, 18·5. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%). It is easily soluble in benzene, acetone, chloroform, and hot acetic acid. It is also slightly soluble in ligroin (b. p. 60—80°).

2-*Nitro*-6-*methyldiphenylamine*-6′-*dibromoarsine* (VII) was prepared and isolated in a similar manner to the preceding compound, hydrobromic acid (36%, 15 c.c.) being used for similar quantities. It crystallised in slender, bronze-orange prisms, m. p. 97—98° after slight softening. Its solubility is generally very similar to that of the corresponding chloro-compound (Found: Br, 34·2. $C_{13}H_{11}O_2N_2Br_2As$ requires Br, 34·6%).

2-Nitro-4-methyldiphenylamine-6′-arsinic Acid (IX).—A mixture of *o*-aminophenylarsinic acid (11·2 g.), 4-bromo-3-nitrotoluene (VIII) (11·2 g.), potassium carbonate (9·0 g.), amyl alcohol (52 c.c.), and a trace of copper powder was boiled for 5 hours. The crude condensation product, isolated as in other cases, crystallised from dilute acetic acid in golden-yellow needles, m. p. 227—229° (decomp.) (Found: As, 21·3. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water, but readily soluble in hot glacial acetic acid. Solutions of the alkali salts are deep red; the magnesium salt is formed only on boiling with magnesia mixture.

2-Nitro-4-methyldiphenylamine-6′-dichloroarsine (X).—The preceding substance (10·3 g.), dissolved in a boiling mixture of alcohol (30 c.c.) and hydrochloric acid (33 c.c.) containing a trace of iodine, was reduced in the usual manner. A heavy oil separated; this was decanted and dissolved in benzene, and the filtered solution dried with calcium chloride. Approximately two-thirds of the solution was reserved for the preparation of the succeeding compound (XI), the remaining portion being concentrated to small bulk. Cautious addition of ligroin (b. p. 60—80°) caused the precipitation of amorphous matter, which was filtered off, and the further addition of ligroin precipitated an oil which was finally obtained crystalline. It was recrystallised from benzene–ligroin, and the *dichloroarsine* thus obtained in short orange-yellow prisms, m. p. 91—93°. It is readily soluble in benzene and acetone and somewhat readily soluble in hot ligroin (Found: Cl, 18·55. $C_{13}H_{11}O_2N_2Cl_2As$ requires Cl, 19·0%).

10-Chloro-4-nitro-2-methyl-5 : 10-dihydrophenarsazine (XI).—The benzene extract reserved in the previous preparation was evaporated to dryness, and the residual oil (approx. 6 g.) boiled in acetic acid solution (65 c.c.) for 3 hours. Hydrogen chloride was evolved, but no solid separated until the solution was cooled. The substance was recrystallised from glacial acetic acid and obtained in deep red needles, m. p. 187—188° after slight softening (Found: Cl, 10·35. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is readily soluble in acetone, benzene, and hot glacial acetic acid and only sparingly soluble in ligroin.

10-Bromo-4-nitro-2-methyl-5 : 10-dihydrophenarsazine.—A hot solution of compound (IX) (6 g.) in a mixture of alcohol (30 c.c.) and hydrobromic acid (*d* 1·265, 30 c.c.) containing a trace of iodine was reduced with sulphur dioxide. An oil and a deep red solid were precipitated. The two were separated by decantation; the red solid had m. p. 180—186°. The oil was readily soluble in benzene, but application of the methods successfully applied to dichloroarsines similarly prepared did not lead to the isolation of

the dibromoarsine in a state of purity. The oil was therefore boiled with acetic acid (45 c.c.) for 3 hours, hydrogen bromide being evolved. On cooling, deep red needles were deposited and on recrystallisation from glacial acetic acid the product was obtained *in deep crimson needles*, m. p. 186—188° (Found: Br, 21·5. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%). The red solid precipitated with the oil was shown to be the same substance. Reduction of 2-nitro-4-methyldiphenylamine-6′-arsinic acid leads therefore to the formation of the dibromoarsine and the ring bromo-compound.

10-*Bromo-4-nitro-2-methyl*-5 : 10-*dihydrophenarsazine* is more soluble in the usual solvents than the corresponding chloro-compound.

4-*Nitro-2-methylphenarsazinic Acid* (XII).—A suspension of the chloro-compound (XI) (2 g.) in acetic acid (20 c.c.) was treated with hydrogen peroxide (20 vols., 13 c.c.) as described in similar oxidations. The crude product readily dissolved in cold dilute sodium hydroxide solution; after being boiled with decolorising charcoal, filtered, acidified, and cooled, the deep red solution yielded the *phenarsazinic acid* as a voluminous yellow precipitate. This crystallised from dilute acetic acid (about 80%) in clusters of fine needles (Found: As, 22·5. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). It decomposes violently at 305°, is insoluble in cold alcohol, slightly soluble in hot alcohol, and apparently insoluble in cold or hot water. Its amphoteric character is demonstrated by the ease with which it dissolves in acetic acid and in a mixture of alcohol and hydrochloric acid. The ammonium salt loses ammonia when its aqueous solution is boiled, the acid being precipitated. When a 20% solution of sodium hydroxide is added to a solution of the acid in dilute aqueous sodium hydroxide, a sodium salt is precipitated in short yellow plates; the hot solution, however, yields a deep brown (*aci* ?) crystalline salt, which changes to the former on cooling. The silver salt is an orange-yellow amorphous substance soluble in ammonia; the barium salt forms small, deep yellow, flat needles, the calcium salt long plates arranged in clusters. The last two salts are very well defined and characteristic.

5-*Nitro-3-methyldiphenylamine-6′-arsinic Acid* (XXXI).—3-Bromo-5-nitrotoluene (XXX) (22·4 g.), condensed under the usual conditions with *o*-aminophenylarsinic acid (22·4 g.), gave an 88% yield of the crude acid. The somewhat tarry product solidified on standing and was then recrystallised from 50% acetic acid (charcoal). After a further recrystallisation, the pure *acid* was obtained in long, pale yellow needles, m. p. 228—230° (decomp.) (Found: As, 21·5. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The ammonium salt is sparingly soluble in an excess of concentrated ammonia solution and its solution in water is deep red. The calcium salt

crystallises in clusters of yellow needles; the barium salt is easily crystallised from hot water and is obtained in glistening yellow plates; the silver, mercurous, mercuric and lead salts are yellow amorphous precipitates; the sodium salt is deep reddish-brown and sparingly soluble in a concentrated solution of sodium hydroxide. The magnesium salt, unlike those of most arsinic acids, is formed in the cold solution in clusters of yellow needles.

10-Chloro-1(or *3*)*-nitro-3*(or *1*)*-methyl-5 : 10-dihydrophenarsazine* (XXXII).—A boiling solution of the preceding acid (10 g.) in alcohol (50 c.c.) and hydrochloric acid (40 c.c.) containing a little iodine, on reduction in the usual manner with sulphur dioxide, gave a good yield of homogeneous material and the mother-liquor gave no further precipitate when resaturated with sulphur dioxide and kept. The melting point of the crude material was 225—228° and this indicated that ring closure had taken place; moreover the material was insoluble in the usual organic solvents and also in *o*-dichlorobenzene and in *s*-tetrachloroethane. It was sparingly soluble in nitrobenzene. It crystallised from butyric acid (the best solvent for purification) in clusters of orange-coloured needles, decomp. 245—247° (Found: Cl, 10·5. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%).

10-*Bromo*-1(or 3)-*nitro*-3(or 1)-*methyl*-5 : 10-*dihydrophenarsazine*.—A boiling solution of the acid (XXXI) (5·3 g.) in alcohol (40 c.c.) and hydrobromic acid (36%, 30 c.c.) containing a little iodine, on reduction in the usual manner, gave a homogeneous deep red product. It was recrystallised from a large volume of acetic acid and obtained in thick red prisms having an indefinite melting point (237—242°), the last portions to separate from the mother-liquor having also the same indefinite melting point (Found: Br, 21·2. $C_{13}H_{10}O_2N_2BrAs$ requires Br, 21·0%).

1(or 3)-*Nitro*-3(or 1)-*methylphenarsazinic Acid*.—The chloro-compound (XXXII) (0·9 g.), suspended in acetic acid (10 c.c.), was gently warmed with hydrogen peroxide (20 vols., 5·0 c.c.), its colour changing to yellow. The mixture was boiled for a few minutes, water (20 c.c.) added, and the yellow solid which separated on cooling was filtered off and dissolved in the minimum quantity of dilute sodium hydroxide solution. After treatment with decolorising charcoal, the filtrate was acidified with the minimum quantity of dilute hydrochloric acid, the *phenarsazinic acid* being precipitated as a gelatinous yellow solid. It crystallised from dilute acetic acid in clusters of short yellow needles, which remained unmelted at 300° (Found: As, 22·05. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The sodium salt is obtained in soft needles sparingly soluble in dilute sodium hydroxide solution.

3-Nitro-4-methyldiphenylamine-6′-arsinic Acid (XXVII).—4-Bromo-2-nitrotoluene (XXVI) (16·8 g.), condensed with *o*-aminophenylarsinic acid (16·8 g.) in the presence of potassium carbonate (13·5 g.), amyl alcohol (78 c.c.) and a trace of copper powder, gave a tarry product which could not be crystallised directly. It was therefore treated in boiling dilute ammonia solution with barium nitrate (the boiling solution must contain free ammonia); the *barium salt* (28·4 g.) then crystallised in golden-yellow, rhomb-shaped plates containing $6H_2O$ (Found: H_2O, 17·3, 17·9. $C_{13}H_{11}O_5N_2AsBa,6H_2O$ requires H_2O, 18·1%). The anhydrous salt is chocolate-brown (Found: Ba, 23·0. $C_{13}H_{11}O_5N_2AsBa$ requires Ba, 23·0%) and readily reverts to the yellow hydrate on warming with water. The free acid was obtained by suspending the barium salt in boiling water, acidifying it with dilute hydrochloric acid, and adding acetic acid to the boiling solution until the latter was homogeneous. After treatment with decolorising charcoal, the filtrate deposited the *arsinic acid* in bright yellow needles, m. p. 165—166° (Found: As, 21·0. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is insoluble in water and readily soluble in boiling acetic acid.

Reduction of 3-Nitro-4-methyldiphenylamine-6′-arsinic Acid.—The preceding substance (4·2 g.), dissolved in a boiling mixture of alcohol (30 c.c.) and hydrochloric acid (20 c.c.) containing a trace of iodine, was reduced with sulphur dioxide. A quantity of orange-yellow material (*A*) separated. This was filtered off and the filtrate was boiled and again saturated with sulphur dioxide. A quantity of red material (*B*) was precipitated. *A* and *B* were separately washed with alcohol and dried on porous porcelain. *A*, almost insoluble in benzene, crystallised from acetic acid in orange-yellow prisms, m. p. 257—258° (decomp.). *B*, readily soluble in hot benzene, crystallised from this solvent in bright red needles, m. p. 225—226° (decomp.). The decomposition point of the mixture was 225—226°. The substances are different not only in colour and crystalline form but also in solubility, *B* being generally much more soluble than *A*. When a mixture of *A* and *B* was dissolved in hot benzene, the two substances crystallised out side by side and could be separated mechanically. From the results of analysis the two substances must be the two isomeric ring condensation compounds [*Found: for A* (probably XXVIII), Cl, 10·2; *for B* (probably XXIX), Cl, 10·15. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%]

1- *and 3-Nitro-2-methylphenarsazinic Acids.*—*Oxidation of substance A.* The chloro-compound (3·3 g.) was heated with acetic acid (33 c.c.) and hydrogen peroxide (20 vols., 15 c.c.). A clear solution resulted while boiling and yellow needles soon began to separate. After 10 minutes' boiling, water (60 c.c.) was added

the precipitated *acid* crystallised from a large volume of dilute acetic acid in minute yellow needles, unmelted at 297° (Found: As, 22·3. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The *barium* salt formed orange-coloured needles; the sodium salt, obtained from a solution in concentrated aqueous sodium hydroxide, formed thin, pale yellow needles.

Oxidation of substance B. This was oxidised in the same way as the above, the two acids and salts being superficially indistinguishable (Found: As, 22·2. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The acid was unmelted at 297°.

4-*Nitro-3-methyldiphenylamine-6′-arsinic Acid* (XXXIV).—The condensation of 3-bromo-6-nitrotoluene (XXXIII) (19·4 g.) with *o*-aminophenylarsinic acid (19·4 g.) in presence of amyl alcohol (90 c.c.), potassium carbonate (15·6 g.), and a trace of copper powder gave a product which was purified as follows. The crude acid (86% yield) was dissolved in hot 20% sodium hydroxide solution and allowed to cool. The sodium salt was filtered off, recrystallised from 20% aqueous sodium hydroxide, and obtained in golden-yellow needles. It was dissolved in hot water and treated with glacial acetic acid until a faint turbidity was produced in the boiling solution; this was then boiled with decolorising charcoal, filtered, and allowed to cool. The *acid* was precipitated usually in pale yellow needles, but occasionally as a gum which solidified on cooling. In the latter case, a little of the acid was used for seeding the solution after it had been reheated and allowed to cool. The acid was finally recrystallised from dilute acetic acid and obtained in pale yellow needles with no definite melting point, ultimately decomposing vigorously at 200° (Found: As, 21·2. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). All the salts appear to be amorphous except the sodium and ammonium salts.

10-*Chloro*-2-*nitro*-1(or 3)-*methyl*-5 : 10-*dihydrophenarsazine* (XXXV).—On reduction of the preceding acid (6 g.), dissolved in a mixture of alcohol (20 c.c.) and hydrochloric acid (20 c.c.), in the usual way, an oil and solid matter were precipitated. The oil solidified on cooling, and the dry solid mass had m. p. 220—228° (decomp.). It was sparingly soluble in benzene and was recrystallised from acetic acid (charcoal), forming orange-yellow prisms, m. p. 236—238° (decomp.) (Found: Cl, 10·7. $C_{13}H_{10}O_2N_2ClAs$ requires Cl, 10·5%). It is moderately easily soluble in acetone, slightly soluble in alcohol and *s*-tetrachloroethane, but insoluble in carbon tetrachloride.

2-*Nitro*-1(or 3)-*methylphenarsazinic Acid* (XXXVI).—The oxidation of the preceding substance (2·6 g.), suspended in acetic acid (26 c.c.), with hydrogen peroxide (13 c.c.) proceeded slowly even

in the boiling solution on account of the sparing solubility of the chloro-compound. After boiling for 5 minutes, it was heated on the water-bath for 30 minutes, water (52 c.c.) added, and the precipitated acid separated from non-acidic substances by solution in alkali. The filtered deep red solution on acidification gave a yellow gelatinous precipitate of the *acid*, which was crystallised from a mixture of acetic acid and dilute hydrochloric acid, forming yellow needles, unmelted at 308°. It was insoluble in water and only slightly soluble in acetic acid (Found: As, 22·45. $C_{13}H_{11}O_4N_2As$ requires As, 22·45%). The calcium and barium salts form pale yellow needles. The salts of the heavy metals are amorphous. The sodium salt gives in water a deep red solution which becomes yellow on dilution; on addition of concentrated sodium hydroxide solution, the red colour is again produced, which again changes to yellow on dilution (compare 2-nitro-4-methylphenarsazinic acid, XX). The sodium salt is precipitated in crimson needles when its hot solution in moderately concentrated aqueous sodium hydroxide is cooled.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON),
LONDON, S.E. 1. [*Received, April 17th, 1929.*]

CLXIV.—*Tertiary Phosphines containing the Higher Alkyl Radicals.*

By WALTER CULE DAVIES, PERCY LEONARD PEARSE, and WILLIAM JACOB JONES.

CAHOURS (*Jahresber.*, 1873, 518) stated that zinc propyl on interaction with phosphorus trichloride gave tripropylphosphine. Attempts by Collie (J., 1888, **53**, 715) to prepare tripropylphosphine, by heating phosphonium iodide with propyl alcohol in sealed tubes, were unsuccessful. However, by distilling propyltriethylphosphonium chloride he obtained propyldiethylphosphine hydrochloride, and similarly, from *iso*amyltriethylphosphonium chloride, *iso*amyldiethylphosphine hydrochloride. Hofmann (*Ber.*, 1873, **6**, 292) obtained small quantities of tri*iso*propyl-, tri*iso*butyl-, and tri*iso*amyl-phosphine, in an impure state, by digesting the secondary phosphine with the corresponding iodide and treating the product with alkali. In a similar manner he prepared the hydriodide of ethyl*iso*propyl*iso*butylphosphine by heating *iso*propyl*iso*butylphosphine with ethyl iodide. Hofmann failed to obtain tertiary bases by heating phosphonium iodide with *iso*butyl and *iso*amyl alcohol, respectively. Moreover, Hofmann (*Phil. Trans.*, 1860, **150**,

412) made unsuccessful attempts to prepare tri*iso*amyl- and triallylphosphine by heating the corresponding iodide with phosphorus and zinc.

None of the preceding methods affords a satisfactory means of preparing tertiary phosphines containing higher alkyl radicals in good yield and in pure condition. For this purpose the use of Grignard reagents is much to be preferred and has already proved to be successful in the case of phosphines containing the *n*-butyl radical (Davies and Jones, this vol., p. 33). This method, however, is restricted, because with the higher alkyl halides the yield of organomagnesium derivative is often poor, and, where Grignard reagents derived from secondary and tertiary alkyl halides are caused to interact with phosphorus halides, side reactions seriously interfere with the yield of tertiary phosphine. In the course of the present investigation tertiary phosphines containing the following alkyl groups have been prepared: *n*-propyl, *iso*butyl, *n*-amyl, β-methylbutyl, γ-methylbutyl (*iso*amyl), and δ-methylamyl (*iso*hexyl).

In the air the trialkylphosphines are directly converted into their oxides, the *n*-series being less readily oxidised than the *iso*-series, whereas phosphines containing aryl groups are unaffected. On analysis by combustion with copper oxide the phosphines give low results for carbon and for hydrogen, particularly if they are not previously thoroughly mixed with powdered copper oxide. No satisfactory results were obtained in estimations of phosphorus, although repeated attempts were made by the following methods: heating the phosphine with fuming nitric acid in a sealed tube, with sodium carbonate in a current of oxygen (compare Bay, *Compt. rend.*, 1908, **146**, 814), with a mixture of concentrated nitric and sulphuric acids, with potassium persulphate and concentrated sulphuric acid (Poggi and Polverini, *Atti R. Accad. Lincei*, 1926, **4**, 315), and with "perhydrol" and concentrated sulphuric acid. Trialkylphosphines combine directly with carbon disulphide to give stable red crystalline compounds, but in the case of the alkylarylphosphines the red compounds formed immediately dissociate completely on being isolated. All the phosphines here described combine with methyl iodide, but difficulty is experienced in obtaining phosphonium halides by combination with the higher alkyl halides.

The method of preparing phosphines adopted in the present investigation is similar to that which has been already described (Davies and Jones, *loc. cit.*), but the proportions of the Grignard reagent and of the phosphorus chloride have been varied according to the yield of organomagnesium halide obtained and to the chlorine-content of the particular phosphorus chloride used.

Experimental.

Tri-n-*propylphosphine* is prepared by the addition of 12 c.c. of phosphorus trichloride in 50 c.c. of ether to a Grignard solution made from 56 c.c. of *n*-propyl bromide, 15 g. of magnesium and 300 c.c. of ether. Yield of purified phosphine, 10 g. B. p. 103·5°/50 mm., 187·5°/760 mm.; $d_{4^\circ}^{25^\circ}$ 0·807 (Found: C, 66·9; H, 13·3; *M*, 161. $C_9H_{21}P$ requires C, 67·4; H, 13·2%; *M*, 160). The *carbon disulphide compound*, $C_9H_{21}P,CS_2$, m. p. 108° (Found: S, 26·9. $C_{10}H_{21}S_2P$ requires S, 27·1%), is prepared by mixing alcoholic solutions of its components, and recrystallised from alcohol. *Tri*-n-*propylphosphine mercurichloride*, m. p. 137°, is obtained by mixing alcoholic solutions of the constituents and repeatedly crystallising the product from glacial acetic acid, the crystals being washed with alcohol and dried. The chlorine-content was determined by heating the compound with sodium carbonate in a combustion tube, dissolving the product in dilute nitric acid, and precipitating silver chloride by addition of silver nitrate (Found: Cl, 16·7. $C_9H_{21}P,HgCl_2$ requires Cl, 16·4%). *Methyltri*-n-*propylphosphonium iodide* (Found: I, 41·5. $C_{10}H_{24}IP$ requires I, 42·0%), m. p. 212·5°, and *tetra*-n-*propylphosphonium bromide* (Found: Br, 28·0. $C_{12}H_{28}BrP$ requires Br, 28·2%), decomposing at 200°, are best recrystallised from alcohol, and their halide content can be determined by solution in water and precipitation with silver nitrate.

Phenyldi-n-*propylphosphine* is prepared by introducing an ethereal solution of 19 c.c. of phenyldichlorophosphine to magnesium *n*-propyl bromide obtained from 36 c.c. of *n*-propyl bromide and 10 g. of magnesium. Yield, 17 g. B. p. 159°/50 mm.; $d_{4^\circ}^{25^\circ}$ 0·925 (Found: C, 73·9; H, 10·0; *M*, 193. $C_{12}H_{19}P$ requires C, 74·2; H, 9·9%; *M*, 194). The *mercuric chloride compound*, m. p. 192·5°, separates as needles from alcohol (Found: Cl, 15·3. $C_{12}H_{19}P,HgCl_2$ requires Cl, 15·2%). *Phenylmethyldi*-n-*propylphosphonium iodide* melts at 137° (Found: I, 37·6. $C_{13}H_{22}IP$ requires I, 37·8%) and can be recrystallised from water. *Phenyltri*-n-*propylphosphonium bromide* has m. p. 131·5° (Found: Br, 24·9. $C_{15}H_{26}BrP$ requires Br, 25·2%).

p-*Tolyldi*-n-*propylphosphine* is obtained by adding 20 c.c. of *p*-tolyldichlorophosphine to magnesium *n*-propyl bromide prepared in ethereal solution from 36 c.c. of *n*-propyl bromide. Yield, 14 g. B. p. 174°/50 mm.; $d_{4^\circ}^{25^\circ}$ 0·921 (Found: C, 74·7; H, 10·3; *M*, 203. $C_{13}H_{21}P$ requires C, 75·0; H, 10·2%; *M*, 208). p-*Tolyldi*-n-*propylphosphine mercurichloride* melts at 129·5°, and is obtained as prisms from glacial acetic acid (Found: Cl, 14·9. $C_{13}H_{21}P,HgCl_2$ requires Cl, 14·8%). p-*Tolylmethyldi*-n-*propylphosphonium iodide*, m. p. 81·5° (Found: I, 36·1. $C_{14}H_{24}IP$ requires I, 36·2%), can be

recrystallised from alcohol. p-*Tolyltri*-n-*propylphosphonium bromide*, m. p. 125·5° (Found : Br, 24·0. $C_{16}H_{28}BrP$ requires Br, 24·1%), is formed with difficulty, and is obtained by refluxing the components in ethereal solution; well-developed, hygroscopic needles crystallise on cooling.

*Triiso*butylphosphine (yield, 12 g.), obtained by the addition of 14 c.c. of phosphorus trichloride to magnesium *iso*butyl bromide prepared from 94 c.c. of *iso*butyl bromide and 20 g. of magnesium, has b. p. 126°/50 mm. (Found : C, 69·7; H, 13·3; *M*, 191. $C_{12}H_{27}P$ requires C, 71·2; H, 13·5%; *M*, 202). The phosphine combines with carbon disulphide, giving highly unstable red crystals. *Triiso*butyl*phosphine mercurichloride*, m. p. 191·5°, is obtained as plates from alcohol (Found: Cl, 14·8. $C_{12}H_{27}P,HgCl_2$ requires Cl, 15·0%). Methyltri*iso*butylphosphonium iodide has already been prepared by Hofmann (*Ber.*, 1873, 6, 300), m. p. 287° (Found : I, 36·8. Calc. for $C_{13}H_{30}IP$: I, 36·8%). It readily crystallises from water, being very soluble in hot water and only slightly in cold.

*Phenyldiiso*butylphosphine is prepared by adding 11 c.c. of phenyldichlorophosphine to the Grignard reagent obtained from 47 c.c. of *iso*butyl bromide and 10 g. of magnesium. Yield, 10 g. B. p. 168°/50 mm.; $d_{4°}^{25°}$ 0·910 (Found : C, 75·4; H, 10·6; *M*, 218. $C_{14}H_{23}P$ requires C, 75·6; H, 10·4%; *M*, 222). The *mercuric chloride compound*, after several recrystallisations from alcohol, from which it forms as needles, melts to a cloudy liquid at 158·5° (Found : Cl, 14·3. $C_{14}H_{23}P,HgCl_2$ requires Cl, 14·4%). *Phenylmethyldiiso*butylphosphonium iodide*, m. p. 166·5°, crystallises as pearly leaflets from water (Found : I, 34·7. $C_{15}H_{26}IP$ requires I, 34·8%).

p-*Tolyldiiso*butylphosphine*, obtained from 15 c.c. of *p*-tolyldichlorophosphine and the Grignard solution prepared from 47 c.c. of *iso*butyl bromide (yield, 6 g.), has b. p. 182·5—184·5°/50 mm. and $d_{4°}^{25°}$ 0·915 (Found : C, 75·0; H, 10·7; *M*, 233. $C_{15}H_{25}P$ requires C, 76·1; H, 10·7%; *M*, 236.) *p*-Tolyldi*iso*butylphosphine mercurichloride is precipitated when alcoholic solutions of its generators are mixed, and on recrystallisation from alcohol forms cubic crystals in poor yield and impure. p-*Tolylmethyldiiso*butylphosphonium iodide* separates as an oil which on long preservation crystallises (Found : I, 32·4. $C_{16}H_{28}IP$ requires I, 33·6%).

Tri-n-*amylphosphine* has b. p. 185·5°/50 mm. and $d_{4°}^{25°}$ 0·820 (Found : C, 73·0; H, 13·7; *M*, 236. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%; *M*, 244), and is prepared by the interaction between 10·5 c.c. of phosphorus trichloride and magnesium *n*-amyl bromide made from 78 c.c. of the bromide and 15 g. of magnesium. Yield, 9 g. *Tri*-n-*amylphosphine carbon disulphide* is prepared in quantitative yield on mixing the constituents in alcoholic solution; m. p. 55°

(Found: C, 60·1; H, 10·4. $C_{16}H_{33}S_2P$ requires C, 59·9; H, 10·4%). The mercurichloride and the methiodide of the phosphine could not be obtained crystalline.

The preparation of *phenyldi*-n-*amylphosphine* is effected by adding 11·5 c.c. of phenyldichlorophosphine to the Grignard solution obtained from 42 c.c. of *n*-amyl bromide and 8 g. of magnesium (yield, 10 g.); b. p. 210°/50 mm., $d_4^{25^\circ}$ 0·902 (Found: C, 76·2; H, 10·9; *M*, 247. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). This phosphine is only partially miscible with absolute ethyl alcohol at 15°. It forms a *compound* with mercuric chloride, m. p. 108°, which crystallises well from alcohol (Found: Cl, 13·4. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldi*-n-*amylphosphonium iodide* forms leaflets from water, m. p. 90·5° (Found: I, 32·2. $C_{17}H_{30}IP$ requires I, 32·4%).

p-*Tolyldi*-n-*amylphosphine* has b. p. 220°/50 mm. and $d_4^{25^\circ}$ 0·898 (Found: C, 76·6; H, 11·4; *M*, 260. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). It is prepared by the addition of 11 c.c. of *p*-tolyldichlorophosphine to magnesium *n*-amyl bromide obtained from 51 c.c. of the bromide and 10 g. of magnesium. Yield, 11 g. This *p*-tolylphosphine is still less completely miscible with absolute ethyl alcohol than the corresponding phenylphosphine. The *compound* with mercuric chloride separates as an oil, which crystallises well from glacial acetic acid. It melts at 112° (Found: Cl, 13·3. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldi*-n-*amylphosphonium iodide* separates as an oil which on long preservation crystallises (Found: I, 30·6. $C_{18}H_{32}IP$ requires I, 31·2%).

Tri(dl-β-*methylbutyl*)*phosphine* was obtained in poor yield by adding 10·5 c.c. of phosphorus trichloride to the Grignard reagent prepared from 77 c.c. of *dl*-β-methylbutyl bromide and 15 g. of magnesium, and has b. p. 113—117°/10 mm. (Found: C, 69·8; H, 13·5. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%).

Phenyldi(dl-β-*methylbutyl*)*phosphine* is prepared by adding 14 c.c. of phenyldichlorophosphine to magnesium *dl*-β-methylbutyl bromide from 51 c.c. of the bromide and 10 g. of magnesium. Yield, 8 g. B. p. 198°/50 mm.; $d_4^{25^\circ}$ 0·906 (Found: C, 76·4; H, 11·0; *M*, 249. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). On mixing the components in alcoholic solution the *mercuric chloride compound* is formed; it is isolated by separating the alcoholic layer from the oil and allowing the alcoholic solution to evaporate; m. p. 120° (Found: Cl, 13·3. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldi*(dl-β-*methylbutyl*)*phosphonium iodide*, m. p. 150°, crystallises as glistening plates from water (Found: I, 32·2. $C_{17}H_{30}IP$ requires I, 32·4%).

The preparation of p-*tolyldi*(dl-β-*methylbutyl*)*phosphine* is carried

out by adding 11 c.c. of *p*-tolyldichlorophosphine to the Grignard reagent made from 51 c.c. of the bromide (yield, 7 g.); b. p. 210—211°/50 mm., $d_4^{25^\circ}$ 0·902 (Found: C, 77·1; H, 11·5; *M*, 266. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). The *mercurichloride*, m. p. 99°, was prepared in a similar manner to the corresponding phenyl compound (Found: Cl, 13·2. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldi*(dl-β-*methylbutyl*)*phosphonium iodide* (Found: I, 31·4. $C_{18}H_{32}IP$ requires I, 31·2%), m. p. 131°, crystallises from water in rods.

Triisoamylphosphine [*tri*(γ-*methylbutyl*)*phosphine*] has b. p. 131°/11 mm. (Found: C, 73·2; H, 13·6; *M*, 237. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%; *M*, 244). It was prepared from 10·5 c.c. of phosphorus trichloride, 78 c.c. of *iso*amyl bromide, and 15 g. of magnesium. The final ethereal solution of the phosphine was dried, and the ether distilled off in an atmosphere of carbon dioxide as already described (Davies and Jones, *loc. cit.*), but, in order to prevent oxidation of the phosphine, the residue was fractionally distilled in a vacuum, and all subsequent manipulations with the phosphine were carried out in an enclosure filled with carbon dioxide, without bringing it into contact with the air. Yield, 9 g. The *carbon disulphide compound*, m. p. 79·5° (Found: C, 60·1; H, 10·4. $C_{16}H_{33}S_2P$ requires C, 59·9; H, 10·4%), is obtainable in good yield as red needles. When ethereal solutions of its generators are mixed, *methyltriisoamylphosphonium iodide* (Found: I, 33·2. $C_{16}H_{36}IP$ requires I, 32·9%) is precipitated as an oil which solidifies on keeping.

Phenyldiisoamylphosphine, b. p. 198·5°/50 mm., $d_4^{25^\circ}$ 0·900, is obtained from 14 c.c. of phenyldichlorophosphine, 52 c.c. of *iso*amyl bromide, and 10 g. of magnesium (yield, 12 g.) (Found: C, 76·9; H, 11·2; *M*, 248. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). The *mercuric chloride compound* forms needles and melts at 152° to a cloudy liquid (Found: Cl, 13·3. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldiisoamylphosphonium iodide*, m. p. 181·5°, forms soft, pearly flakes from water (Found: I, 32·5. $C_{17}H_{30}IP$ requires I, 32·4%).

The preparation of p-*tolyldiisoamylphosphine* is effected by adding 11 c.c. of *p*-tolyldichlorophosphine to the Grignard reagent obtained from 52 c.c. of *iso*amyl bromide and 10 g. of magnesium. It has b. p. 210°/50 mm. and $d_4^{25^\circ}$ 0·894 (Found: C, 77·1; H, 11·2; *M*, 258. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). This phosphine is only partially miscible with ethyl alcohol at 15°. p-*Tolyldiisoamylphosphine mercurichloride* forms as an oil which can be crystallised from glacial acetic acid. The prisms melt at 107° (Found: Cl, 13·3. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldiisoamylphos-*

phonium iodide, m. p. 150° (Found : I, 31·1. $C_{18}H_{32}IP$ requires I 31·2%), readily crystallises from water as hard prisms.

Phenyldi(δ-*methylamyl*)*phosphine* (*phenyldiisohexylphosphine*) is obtained when a solution of 13 c.c. of phenyldichlorophosphine in 100 c.c. of ether is introduced into the Grignard reagent prepared from 60 c.c. of δ-methylamyl bromide, 10 g. of magnesium and 350 c.c. of ether. Yield, 7 g.; b. p. 219°/50 mm. (Found : C, 77·2; H, 11·4. $C_{18}H_{31}P$ requires C, 77·6; H, 11·2%). The δ-methylamyl alcohol used for the preparation of this phosphine was obtained from γ-methylbutyl chloride (*iso*amyl chloride) by the method of Grignard and Tissier (*Compt. rend.*, 1902, **134**, 107). Both *phenylmethyldi*-(δ-*methylamyl*)*phosphonium iodide*, m. p. 146° (Found : I, 30·1. $C_{19}H_{34}IP$ requires I, 30·2%), and *phenylethyldi*(δ-*methylamyl*)-*phosphonium iodide*, m. p. 115·5° (Found : I, 29·0. $C_{20}H_{36}IP$ requires I, 29·2%), crystallise as glistening flakes from water.

p-*Tolyldi*(δ-*methylamyl*)*phosphine*, b. p. 234—235°/50 mm., $d_{4}^{25°}$ 0·888 (Found : C, 77·6; H, 11·5; *M*, 284. $C_{19}H_{33}P$ requires C, 78·0; H, 11·4%; *M*, 292), was prepared by adding a solution of 14 c.c. of *p*-tolyldichlorophosphine in 100 c.c. of ether to the Grignard reagent made as described in the case of the previous phosphine. The *mercurichloride*, m. p. 110·5° (Found : Cl, 12·5. $C_{19}H_{33}P,HgCl_2$ requires Cl, 12·6%), forms prisms from glacial acetic acid. The *methiodide* (Found : I, 29·1. $C_{20}H_{36}IP$ requires I, 29·2%) is difficult to recrystallise.

All the preceding preparations of phosphines have involved the use of the Grignard reagents of bromides derived from primary alcohols. In all cases, however, where organometallic compounds of the secondary bromides, *iso*propyl and *sec.*-butyl bromide, were employed, no yield of tertiary phosphine could be obtained, either when ammonium chloride solution was used as described by Davies and Jones (*loc. cit.*), or when the product was subjected to complete distillation as in the procedure adopted by Hibbert (*Ber.*, 1906, **39**, 161) and by Grüttner and Wiernik (*Ber.*, 1915, **48**, 1477). This failure cannot be attributed to insufficient yield of organomagnesium bromide by these alkyl bromides, and it was equally experienced with phosphorus trichloride, phenyldichlorophosphine and *p*-tolyldichlorophosphine. In all these cases the products obtained were evil-smelling mixtures from which no definite substance was isolated.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
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CLXV.—*Catalytic Influences in Three-Carbon Tautomerism. Part I. Sodium Alkyloxides.*

By George Armand Robert Kon and Reginald Patrick Linstead.

The ionic mechanism of tautomeric change originally suggested by Wislicenus and Brühl and developed by Lapworth (J., 1901, **79**, 1265; 1902, **81**, 1508, *et cet.*) is understood to mean the separation of the " mobile " hydrogen in the form of a proton, leaving an anion in which the negative charge can be redistributed. The anion, on recombining with a proton, will then give rise either to the original compound or to an isomeride according to the changes which have taken place.

The further suggestion has been made by Ingold, Shoppee, and Thorpe (J., 1926, 1477) and developed by Ingold (*Ann. Reports*, 1927, 106 *et seq.*), that the separation of the proton is facilitated by potential intramolecular shifting of covalency electrons (" incipient ionisation ") capable of directing complete changes under suitable conditions (compare Allan, Oxford, Robinson, and Smith, J., 1926, 401) and that the redistribution of the negative charge in the anion is conditioned by similar factors.

On the ionic view, the formation of the active form in a three-carbon * *prototropic change—namely the anion*—will be influenced, apart from structural factors, by the nature of the catalytic medium. The more affinity the medium has for the proton, the more ready will be the tautomeric interconversion. Experimental evidence on this point should be readily obtainable by examining the effect of different catalysts on a given system.

As a preliminary step it was necessary to standardise the conditions under which comparisons of mobility are made; and it was hoped at the same time to elaborate standard conditions for the comparison of the mobilities of different classes of tautomeric compounds. It had already been shown by one of us (Linstead, J., 1927, 2579) that comparisons of mobility could readily be made in a series of unsaturated acids, and it remained to elaborate a suitable method for neutral substances. Those selected as test substances for the purpose were the ketones (I and II, X = COMe)

$$\text{(I.)}\quad CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C{:}CHX \qquad CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH_2X\quad \text{(II.)}$$

* We prefer a nomenclature based on *resultant*, as is customary in the classification of tautomerism, to one based on *mechanism*, *e.g.*, "pentad keto-enol," as suggested by Shoppee (J., 1928, 2566; compare Ingold and Rothstein, this vol., p. 9).

and esters (I and II, X = CO_2Et), the former exhibiting a *high*, and the latter a low degree of mobility. The conditions finally chosen as standard were : one equivalent of *N*-sodium ethoxide at 25°, the reagent being prepared from carefully dried alcohol. The mobility, as in the work on acids, can then be expressed in terms of the velocity coefficient (in minutes), $(k_1 + k_2) \times 10^4$, on the assumption of a unimolecular reversible reaction; or the half-change period, $t_{\frac{1}{2}} = 1/(k_1 + k_2) \cdot \log_e 2$, can be used.

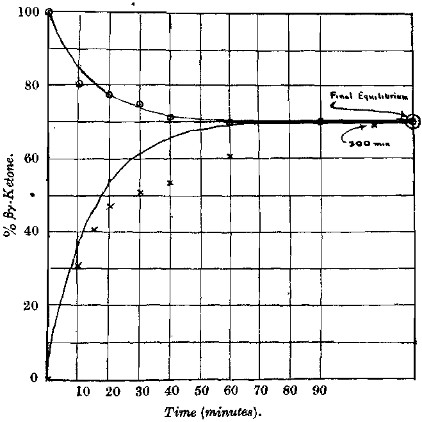
Effect of Sodium Ethoxide on the Ketones.—This reaction has already been studied by Dickins, Hugh, and Kon (J., 1928, 1630), using less than one equivalent of catalyst. It is now found that under the standard conditions both ketones pass rapidly into the equilibrium mixture, which contains 30% of the αβ-form (I). (In these and *subsequent figures we are deliberately neglecting the small amounts of saturated impurity, not separable by fractionation, which are* present.) The rate of equilibration and the point of equilibrium are the same when commercial " absolute " alcohol is used in place of the specially dried solvent, but large amounts of water diminish the rate of equilibration. It is, however, apparent that, whereas the βγ-ketone reaches equilibrium in about 60 minutes, the αβ-ketone takes very much longer. A similar difference is seen in the curves accompanying the previous paper (*loc. cit.*) and also in the figures for the homomesitones (Abbott, Kon, and Satchell, J., 1928, 2514) and can be illustrated by evaluating the equation for a unimolecular reversible change, $k_1 + k_2 = 1/t \cdot \log_e \xi/(\xi - x)$. The change from the βγ-side gives an approximate value for $(k_1 + k_2) \times 10^4 = 700$ with a half-change period of 9·9 minutes. From this the amount of change in time t can be calculated by substituting it in the original equation for the change both from the αβ- and from the βγ-side. The figures so obtained are compared with those found experimentally in Fig. 1. The difference in the rates of equilibration of the two ketones is even more marked when sodium methoxide is employed; in fact an equilibrium mixture is not produced from the αβ-ketone even at the end of 48 hours. The reason for this must be sought in the slow addition of the elements of ethyl (or methyl) alcohol to the αβ-ketone with the production of an ethoxy(or methoxy)-derivative, doubtless of the structure $C_5H_{10}{>}C(OR){\cdot}CH_2{\cdot}COMe$; we have actually isolated such derivatives in both cases. Their formation is slow in comparison with the rate of tautomeric change and can practically be disregarded when one is dealing with the equilibration of the βγ-ketone, as shown by the agreement of the experimental and the calculated curve; the addition product is, however, formed in small amount when the reaction mixture is kept for, say, 20 hours. There is probably a

efinite equilibrium, αβ-ketone + EtOH ⇌ ethoxy-ketone, which ccounts for the small amount of the latter formed.

It is clear from the foregoing that in determinations of the nobility of a system small errors are always to be expected, which vill be minimised by measuring the rate of equilibration of the γ-isomeride.

Effect of Other Alkyloxides.—Sodium methoxide, propoxide and sopropoxide all produce the same equilibrium mixture, containing 0% of αβ- and 70% of βγ-ketone, but the rates of equilibration are

Fig. 1.



Full lines = theoretical curves for $(k_1 + k_2) \times 10^4 = 700$.
⊙ and × = mean observed values from the βγ- and the αβ-side, respectively.

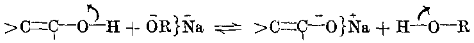
very different. The order of efficiency of these catalysts is *iso*-propoxide>propoxide>ethoxide>methoxide. The activity of the *iso*propoxide could not be compared directly with that of the others, because the strongest solution obtainable was 0·183 *N*; but even this is much more effective than *N*-ethoxide and about equal to *N*-propoxide; a comparison with 0·183 *N*-ethoxide and -propoxide also confirms the order of activity given and is apparent from the approximate times required for half-change (calculated for the αβ-ketone):

Alcohol.	Concentration : $N/1$.	$N \times 0{\cdot}183$.
MeOH	180 mins.	—
EtOH	12 ,,	60 mins.
$Pr^{\alpha}OH$	5 ,,	40 ,,
$Pr^{\beta}OH$	—	9 ,,

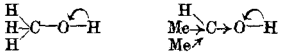
In all these experiments the amounts of ketone and sodium remain constant and the differences are therefore due to the alcohols.*

Such a result can readily be interpreted in the light of the ionic mechanism of tautomeric change and is regarded as significant evidence in support of the views discussed at the beginning of this paper.

The rate of change may be considered as dependent on the concentration of the electromeric anion and hence on the ease of removal of the proton, either in solvated form or, as is more probable in the present case, in combination with the negative alkoxyl ion:



(The ketone is here shown in its enolic form for the sake of simplicity; it is not intended to imply the extent of enolisation.) The extent to which the alkyloxy-ion $\bar{O}R$ will be able to bring about this change will be determined by the toleration of its oxygen atom for the negative charge; the more stable the ion, *i.e.*, the greater the acidity of the alcohol, the less will be its tendency to remove a proton. The difference is well illustrated by comparing methyl alcohol with *iso*propyl alcohol:



In the latter the oxygen has a greater control of the C—O covalency electrons owing to the inductive effect of the two methyl groups and therefore its toleration for the negative charge is lowered (compare Allan and Robinson, J., 1926, 376; Robinson and Smith, *ibid.*, p. 392). The order of the activities of the alkoxyl ion already given is readily deduced from these considerations. The efficiency of the alcohols is the reverse of that expected from their dissociating powers as measured by their dielectric constants.

This explanation is also in good agreement with the observation that *cyclo*hexenylacetone cannot be methylated in presence of methyl alcohol, although it is readily ethylated in presence of ethyl alcohol (Kon, J., 1926, 1792). In the same way, sodium hydroxide

* Since the above was written, Ingold and Shoppee have described a similar difference in the catalytic activities of sodium methoxide and ethoxide (this vol., p. 447, footnote).

should be less effective than sodium methoxide in causing tautomeric interchange, but difficulties arise owing to the fact that the ketone is practically insoluble in water, and, if enough alcohol is added, some of the alkoxyl ion may be formed. The only experiment performed shows that sodium hydroxide in 75% ethyl alcohol is much less effective than sodium ethoxide in its action on the αβ-ketone; a comparison with sodium methoxide is difficult owing to the addition which occurs with the latter.

Effect of Sodium Ethoxide on the Esters.—The conversion of the αβ-ester (I, X = CO_2Et) into a mixture of the two in presence of potassium hydrogen sulphate was shown by Birch, Kon, and Norris (J., 1923, **123**, 1361), and an interconversion in presence of sodium ethoxide at 60° was demonstrated by Linstead and May (J., 1927, 2565), but the point of equilibrium was not known with certainty.

It did not appear practicable to study the effect of sodium alkyloxides other than the ethoxide on the esters owing to the probability of replacement of the ester group.

The action of sodium ethoxide produces a slow equilibration and the rate of change is greatly affected by conditions. For instance, when the pure αβ-ester is treated with sodium ethoxide prepared from commercial absolute alcohol, a gradual change continues for some 250 hours; the mixture then contains 57% of the βγ-ester. At the same time there is considerable hydrolysis with the production of the corresponding acids (I and II, X = CO_2H), and 10% of a higher-boiling neutral fraction is also produced. This contains about half its weight of the β-*ethoxy-ester*, $C_5H_{10}{>}C(OEt){\cdot}CH_2{\cdot}CO_2Et$, formed in the same way as the corresponding ketone.

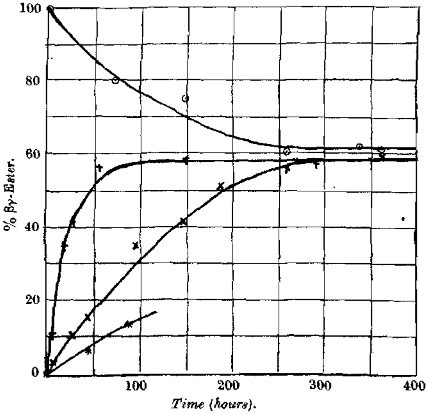
Under similar conditions the βγ-ester gives an equilibrium mixture containing 62% of the βγ-ester; the amount of addition product is very small and considerable hydrolysis again occurs.

The equilibration of the αβ-ester with sodium ethoxide prepared from specially dried alcohol gives the same final position of equilibrium (67% βγ-), but this value is attained in 63 hours. The same small amount of addition product is found, but the extent of hydrolysis is greatly reduced, being only 9% in 6 days and 16% in 12 days. Conversely, the addition of 0·5% of water to the ordinary absolute alcohol greatly increases hydrolysis and retards tautomeric change. These results are illustrated in Fig. 2.

In the light of the experiments on ketones, the retarding effect of water in the present instance is not attributed to a specific anticatalytic action but merely to greatly increased hydrolysis which removes both the ester and the catalyst and thus rapidly decreases the concentration of the reactants; it is significant that the presence of water does not affect the final equilibrium point.

The $\beta\gamma$-ester appears to be hydrolysed more rapidly than the $\alpha\beta$, and there is always more $\beta\gamma$-acid in the mixed acids than $\beta\gamma$-ester in the neutral portion in the same experiments. This does not, however, affect the equilibrium (compare above) and we can therefore suppose that tautomeric change is more rapid than hydrolysis or, alternatively, the rates of hydrolysis of the two esters are of the same order as the proportion of the esters in the equilibrium mixture (4 : 6).

FIG. 2.



⊙ *βγ-Ester + absolute alcohol.* † *αβ-Ester + anhydrous alcohol.*
× *αβ-Ester + absolute alcohol.* * *αβ-Ester + 99·5% alcohol.*

The ethoxy-ester is formed rapidly although in small amount, and this does not increase appreciably on standing; apparently an equilibrium is rapidly set up between the ethoxy- and the $\alpha\beta$-ester and is not disturbed.

The ethoxy-ester has been isolated in a pure state by repeated fractionation and hydrolysed to the corresponding solid acid; we have not yet demonstrated the position of the ethoxy-group with certainty, although it is presumably on the β-carbon. The ethoxy-ester boils some 15° higher than the $\alpha\beta$-ester and shows a definite though small reaction with iodine chloride; its presence in somewhat greater amount in the equilibrium mixture obtained from the

αβ-side is understandable and probably accounts for the slightly divergent equilibrium values found from the two sides.

The true equilibrium is considered to be that found from the βγ-side, namely 62% of βγ-ester. The mobility is $(k_1 + k_2) \times 10^4 =$ 8·1 (in minutes), with a half-change period of 14·1 hours.

The *correctness of the figures obtained for the equilibrium from* the αβ-side was confirmed by the hydrolysis of an ester with an iodine addition corresponding to an αβ-content of 43·5%, under conditions precluding isomeric change. The acid obtained had an iodine addition corresponding to an αβ-content of 42%. The reversibility of the change was also confirmed satisfactorily by the isolation of pure βγ-acid from an equilibrated αβ-ester and of pure αβ-acid from an equilibrated βγ-ester (p. 1280).

EXPERIMENTAL.

A. *Ketones.*

*cyclo*Hexylideneacetone (I, X = COMe) was prepared as described by Dickins, Hugh, and Kon (*loc. cit.*) and purified by fractionation. The specimen used had b. p. 83—84°/12 mm., $d_{4^\circ}^{15\cdot6^\circ}$ 0·95188, $n_D^{15\cdot6^\circ}$ 1·49224, whence $[R_L]_D = 42\cdot11$. *cyclo*Hexenylacetone (II, X = COMe) was regenerated from the semicarbazone and treated with aluminium amalgam (compare Abbott, Kon, and Satchell, *loc. cit.*), the product having a somewhat higher iodine addition than the best previously obtained; it had b. p. 77°/11 mm., $d_{4^\circ}^{19\cdot0^\circ}$ 0·93760, $n_D^{19\cdot0^\circ}$ 1·47389, whence $[R_L]_D = 41\cdot39$. The alcohols used were dehydrated by digesting them twice with calcium (Winkler, *Ber.*, 1905, **38**, 3612).

Procedure.—A weighed quantity of the ketone, and the requisite amount of a titrated solution of sodium in the appropriate alcohol (slightly stronger than normal), together with the additional quantity of the alcohol required to bring the concentration to normal, were separately brought to 25° (thermostat), and then thoroughly mixed. At intervals, test portions, containing 1·5—2 g. of the ketone, were run into 200 c.c. of water containing enough acetic acid to neutralise the alkali formed, and the ketone was twice extracted with ether. The extract (about 150 c.c.) was shaken four times with an equal volume of water and dried over calcium chloride and the ether was removed through a column; the residue was distilled under reduced pressure, a fraction covering the b. p.'s of both ketones being collected. The yields were good (over 80%). The fractions were analysed iodometrically by the method of Linstead and May (*loc. cit.*). A new reference curve was constructed from the following values:

% αβ-Ketone	100	90	75	50	25	10	0
% Iodine addition ...	16·9	26·6	41·0	62·0	77·6	83·4	85·8

Accuracy of the Method.—In some experiments the test portions were halved and the ketone in each half was isolated and analysed separately as a check on the accuracy of the method (Expts. 16 and 17, Table I). The values did not diverge by more than 0·5% in the iodine addition. The agreement between corresponding values obtained in different experiments is of the order of ± 1% (compare Table I).

Table I gives the results obtained. There is no difference, within the limits of experimental error, between the effect of sodium ethoxide prepared from dry (Expts. 1—3) and commercial "absolute" alcohol (Expts. 4 and 5).

The strongest solution of sodium in *iso*propyl alcohol which did not deposit solid sodium *iso*propoxide was about $N/5$; in order to ensure a comparison with sodium ethoxide and propoxide, a series of experiments (8—10) was carried out with 0·183 N-solutions of sodium in the appropriate alcohol. These experiments suffice to show the order of the reaction and incidentally illustrate the effect of dilution.

The point of equilibrium was determined for each alcohol separately and the agreement is satisfactory, the value being 30% of αβ-ketone. The equilibrium mixture derived from the αβ-ketone was also analysed (Found: C, 77·6; H, 10·1. Calc. for $C_9H_{14}O$: C, 78·2; H, 10·2%).

The high fraction obtained from the sodium ethoxide experiments was redistilled; a definite fraction, b. p. 99—101°/9 mm., was obtained which appeared to consist of 30% of unsaturated ketone and 70% of *ethoxy-ketone* (Found: C, 73·3; H, 10·5. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·9%). When treated with semicarbazide, it gave the *semicarbazone* of 1-ethoxy*cyclo*hexylacetone, which formed fine plates, m. p. 174°, from methyl alcohol (Found: C, 59·5; H, 9·4. $C_{12}H_{23}O_2N_3$ requires C, 59·7; H, 9·6%).

A similar high fraction was obtained in the sodium methoxide experiments; the *semicarbazone* of the methoxy-ketone isolated from it formed plates, m. p. 181—182° (Found: C, 57·9; H, 9·3. $C_{11}H_{21}O_2N_3$ requires C, 58·1; H, 9·3%).

B. *Esters.*

Materials.—Ethyl *cyclo*hexylideneacetate (I, X = CO_2Et) was prepared from the corresponding acid either through the acid chloride—the product then contained sub-analytical traces of chlorine—or by boiling with 4% alcoholic hydrogen chloride for 2½ hours. Ethyl Δ^1-*cyclo*hexenylacetate (II, X = CO_2Et) was prepared from the corresponding acid through the acid chloride or by keeping it at room temperature with twice its volume of

TABLE I.

Equilibration of Ketones.

Expt.	Reagent.	Material.	Time (mins.) 10	15	20	30	40	60
1	*N*-NaOEt anhydrous	$\alpha\beta$	—	—	—	—	—	69·0
2	,, ,,	$\alpha\beta$	Lost	*54·1*	*59·4*	61·9	64·9	—
3	,, ,,	$\alpha\beta$	45·2	—	59·0	—	65·8	68·5
4	,, {from commercial abso-	$\alpha\beta$	47·9	—	60·0	62·2	64·1	—
5	,, lute alcohol}	$\alpha\beta$	47·6	—	—	—	—	69·1
6	*N*-NaOPr$^{\alpha}$ anhydrous	$\alpha\beta$	64·6	—	*67·5*	73·6	—	—
7	,, ,,	$\alpha\beta$	—	—	—	*74·8*	—	—
8	0·183*N*-NaOPr$^{\alpha}$ anhydrous	$\alpha\beta$	27·4	—	37·2	—	—	—
9	,, NaOPr$^{\beta}$,,	$\alpha\beta$	51·1	—	63·7	—	—	—
10	,, NaOEt ,,	$\alpha\beta$	Lost	—	28·1	—	—	—
11	*N*-NaOEt anhydrous	$\beta\gamma$	80·2	—	78·7	77·5	75·3 *74·9*	*74·4* (90 minutes)

Expt.	Reagent.	Material.	Time (mins.) 60	120	240	360
12	*N*-NaOMe anhydrous	$\alpha\beta$	41·5	44·7	55·1	60·0
13	,, ,,	$\beta\gamma$	—	79·4	77·0	*74·3*

Other experiments.

Expt.	Reagent.	Material.	
14	*N*-NaOH in 75% EtOH	$\alpha\beta$	60·3 (95 minutes)
15	,, (approx) NaOPr$^{\beta}$	$\alpha\beta$	*74·8* (360 minutes)
16	,, NaOPr$^{\alpha}$ [combined fractions of (6)]		*74·5*, *74·5* (240 minutes)
17	,, NaOEt ,, ,, ,, (2) and (4)		73·7, 73·2 (300 minutes)
18	,, ,, ,, ,, ,, (3)		*74·6* (1200 minutes)
19	,, NaOMe ,, ,, ,, (12)		66·5 (3200 minutes)
20	,, ,, ,, ,, ,, (13)		*74·2* (1440 minutes)

The figures refer to iodine additions. Those italicised represent equilibrium values. The mean figures in Expts. 1, 2, 3, 4, 5, and 11 were used in plotting Fig. 1.

N-alcoholic hydrogen chloride and six times its volume of absolute alcohol for 4 hours. The properties of these esters were as follows :

Ester.	Preparation.	$n_D^{t°}$.	$D_{4°}^{t°}$.	B. p.	% *Iodine* addition.
$\alpha\beta$ (1)	Alcoholic HCl	1·47986/17·9°	0·9829/17·9°	112—114°/16 mm.	7·4
$\alpha\beta$ (2)	Acid chloride	1·47986/18·0	0·9877/18	114·5—115·5/14	6·9
$\alpha\beta$ (3)	Acid chloride	1·47880/18·0	0·9857/18	108/13	7·3
$\beta\gamma$ (1)	Acid chloride	1·4621/24·3	—	113—114/26	75·8
$\beta\gamma$ (2)	Alcoholic HCl	1·4639/18·0	0·9785/18	98/13	76·3

The iodine additions given in this section refer to the % addition in 60 minutes under the conditions of Linstead and May (*loc. cit.*, p. 2578).

In the present work the three preparations of the $\alpha\beta$-ester were mixed, also the two of the $\beta\gamma$-ester (Found : for the $\alpha\beta$-ester, C, 71·1 ; H, 9·3 ; for the $\beta\gamma$-ester, C, 70·9 ; H, 9·4. Calc. : C, 71·4 ; H, 9·6%). Mixtures of the $\alpha\beta$(1)- and the $\beta\gamma$(2)-ester gave the following iodine additions, which were used in plotting the reference curve :

% $\alpha\beta$-Ester	75	60	50	40	33·3	20	14·3
% Addition	29·4	41·8	49·6	56·8	61·0	68·8	71·7

Action of Sodium Ethoxide on the Esters.—A weighed quantity of the ester was treated with an equivalent amount of sodium ethoxide (in the form of a solution slightly stronger than normal) as described for the ketones. In general, about 10 g. of ester were used in each experiment. The reaction was allowed to proceed at 25° in a thermostat. After a suitable interval of time a portion of the solution (v c.c.), with an ester content of 3—6 g., was withdrawn, immediately treated with N/2-sulphuric acid ($3v$ c.c.), and then extracted with ether ($6v$ c.c.) in three portions. The united extracts were freed from ether and the residue was heated on the steam-bath for ½ hour to remove the bulk of the alcohol. The residual oil was shaken with 100 c.c. of 10% sodium carbonate solution until effervescence ceased ; the neutral portion was then extracted with ether ($6v$ c.c.), the extract dried and freed from solvent, and the residue fractionally distilled under reduced pressure, the apparatus used being the same throughout the work. None of the material boiled below the boiling range of the unsaturated esters. The liquid boiling above 115°/14 mm. was collected separately and is referred to in Table II as "ethoxy-ester fraction," although it contained a considerable amount of unsaturated esters. The sodium carbonate extract of the neutral substance was extracted once more with ether to remove traces of ester, acidified, and thoroughly extracted with ether. The dried solution was freed from solvent on the steam-bath and finally in a vacuum desiccator.

TABLE II.

Action of Sodium Ethoxide on Esters.

Initial ester.	Time (hours).	Amount used (g.).	Acid product. G.	Acid product. Composition, % $\beta\gamma$.	Neutral product. Ethoxy-ester fraction (g.).	Neutral product. Unsaturated ester. G.	Neutral product. Unsaturated ester. B. p. °/14 mm.	$n_D^{t°}$.	$d_{4°}^{t°}$.	% Iodine addition.	% $\beta\gamma$ Ester.
1 $\alpha\beta$	6·72	3·25	—	—	0·2 (6%)	2·0 (62%)	102—111°	1·4763/19·1°	0·9777	10·3	3
2 $\alpha\beta$	28·75	3·27	—	—	0·25 (8%)	1·6 (49%)	98—111	1·4698/24·3	0·9747	17·7	11
3 $\alpha\beta$	45	3·33	1·4 (51%)	65	0·2 (6%)	1·2 (36%)	104—115	1·4703/16·8	—	21·5	15·5
4 $\alpha\beta$	97·25	3·27	1·75(33%)	64	0·25 (8%)	1·7 (52%)	91—106	1·4618/24·2	0·9753	38·6	36
5 $\alpha\beta$	144·5	3·54	—	—	—	1·1 (31%)	91—113	1·4606/24·0	0·9730	43·2	41·5
6 $\alpha\beta$	185	5·28	2·1 (40%)	62	0·35 (7%)	2·4 (45%)	100—116	1·4632/18·4	0·9787	48·4	50·5
7 $\alpha\beta$	266	4·75	—	—	0·2 (4%)	1·5 (32%)	105—114	1·4598/21·6	0·9747	54·2	56
8 $\alpha\beta$	360	4·75	—	—	0·35 (7%)	1·4 (30%)	103—113	1·4626/19·8	0·9760	50·0	59
9 $\alpha\beta$	8	3·31	Nil	—	Nil	1·9 (58%)	104—115	1·4750/16·8	—	19·6	13
10 $\alpha\beta$	17	5·43	Trace	—	0·2 (4%)	4·25(78%)	98—108	1·4695/19·5	0·9786	37·9	35
11 $\alpha\beta$	28·75	5·22	,,	—	0·2 (4%)	3·35(64%)	100—112	1·4670/20·3	0·9778	43·0	41·5
12 $\alpha\beta$	63·5	5·43	,,	—	0·75(13%)	4·0 (74%)	95—110	1·4643/19·5	0·9794	54·5	56·5
13 $\alpha\beta$	148	5·22	0·4 (9%)	—	0·7 (13%)	3·4 (65%)	103—116	1·4654/17·0	—	56·0	59
14 $\alpha\beta$	290	6·61	0·9 (16%)	78	0·7 (11%)	4·52(69%)	98—115	1·4645/16·7	0·9822	54·5	56·5
15 $\alpha\beta$	45	3·20	—	—	Nil	0·8 (25%)	104—112	1·4724/15·2	0·9843	13·7	6·5
16 $\alpha\beta$	90	3·20	—	—	,,	0·7 (22%)	104—108	1·4685/13·8	0·9855	20·3	14·5
17 $\beta\gamma$	70	3·74	1·4 (45%)	94	0·1 (2%)	1·3 (35%)	96—116	1·4656/17·0	—	69·1	80
18 $\beta\gamma$	148·5	3·74	1·5 (48%)	91	0·12 (3%)	1·3 (35%)	93—115	1·4653/16·7	0·9788	60·2	75·5
19 $\beta\gamma$	266	3·26	—	—	0·3 (9%)	1·9 (58%)	103—116	1·4630/19·4	0·9770	57·6	61
20 $\beta\gamma$	337	7·92	3·5 (53%)	90	0·2 (3%)	2·62(33%)	94—115	1·4643/16·7	0·9822	58·6	62·5
21 $\beta\gamma$	360	3·26	—	—	0·3 (9%)	1·5 (46%)	102—112	1·4630/19·7	0·9757	58·0	61·5

The alcohol used in these experiments was: (1—8) commercial absolute alcohol; (9—14) anhydrous alcohol; (15—16) absolute alcohol + ½% of water; (17—21) commercial absolute alcohol.

Examination of the Products.—The neutral distillates—main and high fractions—were weighed and the physical properties and iodine addition of the main fraction were taken. In several cases the neutral product was distilled in two portions, the results obtained agreeing closely. The acid product was weighed and, where the amount was sufficient, the iodine value was determined by Linstead and May's interpolation method (*loc. cit.*, p. 2568). In these determinations the alkaline solutions were acidified before titration (*loc. cit.*, footnote, p. 2574) and it was therefore necessary to construct a new reference curve, mixtures of the two pure acids (I and II, X = CO_2H) being used. The figures obtained under the new conditions for a 10-minute reaction were:

% αβ-Acid ...	100	80	50	33·3	25	10	0 (βγ-acid)
% Addition ...	1·0	18·0	35	45·3	48·2	54·0	55·6

The results are summarised in Table II and the main inferences from them have already been made.

Purity of the Unsaturated Ester Fraction.—The refractive index of the ester drops progressively on equilibration (column 10) and the mean value for the equilibrated product (1·4643/17°) is almost identical with that of the βγ-form. This is an indication of the presence of the less refractive ethoxy-ester which is confirmed by analysis [Found: (Expt. 12) C, 70·0, 70·1; H, 9·7, 9·8%]. The figures in the last column are obtained from the iodine addition of the corresponding unsaturated ester fraction by means of the reference figures given on p. 1278. It is obvious that if this fraction contains saturated impurity the observed iodine addition will give an almost correct value for the βγ-content, but will be unable to distinguish between the two non-reactive substances present. Hence the values in the last column in Table II represent the percentage of βγ-ester in the total product and the true percentage—in equilibrium with αβ-ester—will be greater than this. On the other hand, a small amount of unsaturated ester is undoubtedly present in the ethoxy-ester fraction, and of the two unsaturated esters there will be a larger proportion of the higher-boiling αβ-ester in this fraction than in the main fraction in the corresponding experiment. Hence, on this basis, the observed αβ-content in the unsaturated ester fraction will be too low. As the former source of error probably exceeds the latter, the recorded percentage of αβ-ester in the equilibrium mixture represents a maximum.

Hydrolysis of the Equilibrated Esters.—In order to confirm the essential change αβ-ester ⇌ βγ-ester, the equilibrated αβ-ester was hydrolysed to the βγ-acid, and the equilibrated βγ-ester to the αβ-acid. (1) The αβ-ester (6·67 g.) was equilibrated for 381 hours

in the usual way. The neutral product was fractionated twice and a fraction of b. p. 102—105°/16 mm. finally collected. This was hydrolysed with 50% excess of 10% sodium hydroxide solution in the cold for 24 hours, alcohol being added until the mixture was homogeneous (compare Linstead, J., 1927, 2579). The acid fraction was isolated in the usual way and solidified almost completely in a vacuum desiccator. The acid melted at 35—37° alone and at 37—38° when mixed with pure Δ^1-*cyclo*hexenylacetic acid. (2) A sample of equilibrated βγ-ester (Expt. 20, Table II) was refractionated, and the fraction boiling at 112—114°/15 mm. hydrolysed by the method given above. When the alkaline liquid was acidified, *cyclo*hexylideneacetic acid crystallised in long needles, which, alone or when mixed with an authentic sample, melted at 90—91°.

To confirm the composition of the equilibrium mixture of esters, a sample (3·8 g.) obtained from the αβ-ester (Expt. 14, Table II) was hydrolysed with 120 c.c. of 10% sodium hydroxide solution in the manner already described, 3·0 g. of a liquid mixture of acids being obtained. This had an iodine addition of 41·2%, corresponding to an αβ-content of 42%, which agrees well with that (43·5% of αβ) obtained by analysis of the original ester. The nature of the acids was confirmed by treating the mixture with a concentrated solution of iodine under Bougault's conditions (*Ann. Chim. Phys.*, 1908, **14**, 145): 0·80 g. of the mixture then gave 0·16 g. of the αβ-acid (20%) (m. p. and mixed m. p. 90—91°) and 0·85 g. (60%) of the γ-lactone of 1-iodo-2-hydroxy*cyclo*hexyl-1-acetic acid (m. p. 56°, alone or when mixed with a specimen prepared from authentic βγ-acid). These substances were isolated by the method previously used (Linstead and May, *loc. cit.*).

The Acid Products.—In the earlier experiments (1, 2, 5, 7, and 8) the acid products obtained by the hydrolysis of the esters during equilibration were not collected separately (this accounts for the gaps in Table II) but were accumulated in bulk. The mixture so obtained, which was completely soluble in sodium bicarbonate solution, did not solidify in a vacuum desiccator and when fractionated (5 g.) under reduced pressure boiled entirely within the range of the two unsaturated acids. Two fractions were obtained: (1) 145°/22 mm.—150°/17 mm. (2·5 g.) and (2) 150°/17 mm.—158°/21 mm. (1·6 g.). Fraction (1) in ice gave plates of the βγ-acid, m. p. 37°; fraction (2) on long standing gave the αβ-acid as a crystalline powder, m. p. 86—88°, and on subsequent cooling in ice gave the βγ-acid.

In subsequent experiments in which the acid fractions were isolated separately the product often wholly or partly solidified after complete removal of the solvent (Expts. 6, 14, 17, 18, and 20).

In every case the solid was the $\beta\gamma$-acid (m. p. 37°). These results support those obtained from analysis by the iodine method.

The Ethoxy-ester Fraction.—This was accumulated, and the whole distilled from a Claisen flask with a fractionating column in the side arm. The fraction boiling above 121°/15 mm. (2·1 g.) was collected separately and redistilled; 1·7 g. were then obtained, boiling steadily at 128°/15 mm. This was pure *ethyl* 1-*ethoxy*cyclo*hexylacetate* (Found: C, 67·2; H, 10·2. $C_{12}H_{22}O_3$ requires C, 67·2; H, 10·4%). The ester is a colourless liquid noticeably less mobile and less odorous than the unsaturated esters. It has b. p. 122°/11 mm., $n_D^{17.4°}$ 1·45753, $d_4^{17.4°}$ 0·9865. Under standard conditions it has a slight reaction with iodine chloride (13·4%).

Hydrolysis of the ester with potassium hydroxide gave a good yield of the corresponding acid, m. p. 43°; recrystallised from ether, this formed flattened needles, m. p. 50—51°. It was immediately soluble in aqueous sodium bicarbonate, and the solution did not reduce permanganate. The *silver* salt was appreciably soluble in hot water, from which it crystallised in fine needles, m. p. 216° (decomp.) (Found: Ag, 37·0. $C_{10}H_{17}O_3Ag$ requires Ag, 36·8%).

In an attempt to confirm the β-position of the ethoxyl group (assumed above) the ester was heated in a sealed tube with a solution of hydrogen bromide in acetic acid for 2 hours. The product was evaporated on the steam-bath and left in a vacuum desiccator over potassium hydroxide. A white crystalline solid remained, m. p. 60°. Owing to the extremely small amount available it was not possible to recrystallise this and confirm its identity with 1-bromo-1-*cyclo*hexylacetic acid (m. p. 90°). The fact that a solid acid and not a liquid lactone was obtained, however, indicates that the ethoxyl group in the original ester is in the β-position to the carbethoxyl group.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CLXVI.—*The Walden Inversion. Part II.*

By HANS NICOLAI KELLERMANN RÖRDAM.

IN a former paper (J., 1928, 2447) the author set forth a new hypothesis of the reaction mechanism of the Walden inversion, the fundamental assumption being that the optically active molecule,

after splitting off one of the radicals linked to the asymmetric carbon atom, oscillates between two configurations, each of which, by the addition of a new radical, will produce only one of the two possible optical antipodes. A rigid mathematical treatment of this hypothesis would undoubtedly be very complicated, but by making certain simplifying assumptions, it was shown to lead to the equation

$$n = k.c_x.F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this formula, n denotes that fraction of the reaction product which retains its original configuration, c_x the mean of the concentrations of the entering radical at the beginning and at the end of the reaction, F the kinetic activity factor of Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169), and k a constant.

It is obvious that the above equation entails an unlimited increase of n by increasing c_x, whereas actually, of course, n can only vary from zero to unity; but this only means that, as a first approximation, a straight line has been substituted for the unknown theoretically correct curve. The application of equation (1) to some of the most accurate experiments upon the Walden inversion hitherto reported showed, in general, very good agreement between theory and experiment.

A number of Walden inversions now described were carried out under experimental conditions such as to conform as closely as possible to the requirements of the theory, and it will be seen that up to $c_x = 0{\cdot}4M$ the experimentally found values agree with great accuracy with the linear variation of n demanded by the simplified equation, whilst for greater variation in c_x the anticipated bending of the curve is realised. The immediate aim of this research is to accumulate sufficiently accurate data upon the Walden inversion; the deduction of a complete theory will be relegated to a later paper.

From the point of view of the new hypothesis we must postulate the existence of two distinct types of these inversions, depending upon the character of the non-asymmetric component in the reaction.

Type 1. Reactions where the splitting of the optically active molecule either occurs spontaneously or is caused by some molecule which is neither identical with nor contains the entering radical. In this type, both *d*- and *l*-forms are produced in amounts which depend upon the concentrations, and theoretical calculation of the stereochemical inhomogeneity of the reaction product based upon the views of the new hypothesis can therefore be applied. Besides the reaction between bromosuccinic acid and xanthogenates, to which the theory was applied in Part I (*loc. cit.*), we must include in this type all reactions where halogen linked to an asymmetric carbon atom is replaced by hydroxyl or by other radicals present

in the solution in the state of ions, as well as reactions where a hydroxyl group linked to an asymmetric carbon atom is replaced by the influence of halogen ions.

Type 2. This type comprises *reactions where the splitting of the* optically active molecule is brought about by a molecule containing the radical which displaces the ejected radical. This we must assume to be the case when the replacement of a hydroxyl group linked to an asymmetric carbon atom is caused by reagents such as phosphorus pentachloride, thionyl chloride, nitrosyl bromide, etc. In these cases it seems natural to follow the customary view which assumes that an addition or some very near position of the halogeno-compound molecule causes the splitting off of the hydroxyl group; and a similar mechanism must be assumed if a halogen atom linked to an asymmetric carbon atom reacts with a molecule of water or ammonia, producing an exchange of halogen for a hydroxyl or amino-group. Another example is afforded by the reaction between a nitrous acid molecule and an active amino-compound.

In such cases the entering radical must, at the moment of the splitting of the active molecule, always be very nearly at the same distance from the vacant place at the asymmetric carbon atom—a distance which depends upon the nature of the reacting molecules but is independent of the concentrations—and consequently the entering radical will always occupy very nearly the same time in taking that vacant place. The word "nearly" is used in the foregoing sentences because the addition may perhaps take place in slightly different ways even for the same reagent. Whether the replacement occurs in the first or in a later phase of the oscillation (*i.e.*, whether it does not or does produce inversion) will depend upon the structure of the molecules and the period of the oscillation, but as these quantities have constant values, we must expect that only one *stereochemical form of the reaction product will result, and this* type of Walden inversion is consequently not amenable to calculation of the composition of the reaction product. Of course, it is possible that accidental and uncontrollable influences, such as casual shocks from the surrounding molecules of the solvent, may cause divergencies, but in the main it seems natural to ascribe racemisation, if occurring in greater degree in reactions of this type, to secondary influences not directly connected with the double decomposition.

Finally, we must also expect that reactions may occur which represent a transition stage between the two types, or which actually proceed simultaneously in the two different typical ways. Such an example is perhaps to be found in the processes which are usually attributed to the action of nitrosyl bromide upon active amino-compounds, although such reactions may be due both to (i) the

undissociated nitrosyl bromide molecules and to (ii) nitrous acid and bromine ions. From the views given above, we should expect the first of these processes to give only one stereochemical form and the other to give both the *d*- and the *l*-form of the resulting halogen compound. The results of this process reported in the literature seem to justify this explanation.

In the foregoing systematic classification, we have only taken account of the nature of the optically inactive component of the reaction, but that the nature of the optically active compound plays a considerable part in determining the stereochemical course of the process is well known, since, for example, an optically active ester and the corresponding free acid in some cases give different stereochemical forms of the reaction product with the same reagent. Apart from the influence of concentration and other experimental conditions, this phenomenon may be a direct consequence of the hypothesis now advanced, since the time of oscillation must necessarily be different for an ester and for its free acid—or, to take an example of another type, for bromopropionylglycine and for the free bromopropionic acid (Fischer, *Ber.*, 1907, **40**, 489)—and if this difference is great enough, the two reactions can give rise to products of opposite sign.

Another important influence arises from the well-known fact that only in exceptional cases can the asymmetric carbon atom be assumed to occupy the centre of a perfectly regular tetrahedron, for generally the tetrahedron is more or less irregular. This point is of importance primarily for the mathematical treatment of our hypothesis; here it is only necessary to mention that, whilst in the diagrammatical case of a regular tetrahedron, the period of the first phase of the oscillation must be half that of each of the following phases, yet in all actual cases this ratio can be either greater or less than one-half.

The present paper describes the first of a series of researches, designed from the point of view of the author's hypothesis, upon the mechanism of the Walden inversion; and a process of Type 1 has been chosen in order to investigate the influence upon it of systematic variation of (*a*) the concentration, the ionic strength μ (and consequently also the activity factor F) being kept constant, and (*b*) the ionic strength, the concentration being kept constant.

As the reaction between halogeno-succinic acids and xanthogenates has been shown by Holmberg (see Part I, *loc. cit.*) to proceed in a well-defined way, *l*-bromosuccinic acid and potassium xanthogenate were chosen for my purpose. It is assumed (see Part I, *loc. cit.*) that *l*-bromo- and *d*-xanthogeno-succinic acids have the same configuration, and this raises a point of fundamental importance.

When a radical linked to an asymmetric carbon atom is replaced by another radical, there is as yet no means of ascertaining *with certainty* which of the two possible forms of the reaction product has the same configuration as the original molecule; for, when an optically active molecule is transformed under different conditions (but without interference from other optically active molecules) into oppositely rotating forms of the same reaction product, all we can say is that a Walden inversion has taken place *in one of these reactions*. The literature contains numerous instances in which a Walden inversion is said to have taken place with or without a change in the sign of rotation, but these are necessarily only expressions of opinion in the light of various hypotheses, and the same applies to the present statement as to the bromo- and xanthogenosuccinic acids. The conception of the Walden inversion advocated here and in Part I leads to the conclusion that, in reactions of Type 1, that form of the reaction product which increases in amount with increasing concentration of the entering radical in the solution has the same configuration as the original substance. Moreover, if valid, this theory for reactions of Type 1 affords a means, hitherto lacking, of deciding which forms of related substances have corresponding configurations.

The results of the two types of experiment (*a*) and (*b*) are shown in Tables I and II and Figs. 1 and 2, respectively, *n* being recorded as a percentage of *d*-acid formed. When the values of *n* in Expts. 6—10 are multiplied by the factor 48·9/43·6, *i.e.*, the ratio of the values in Expts. 11 and 10, we get those values of *n* which would

TABLE I.

(Bs = Bromosuccinic radical; X = xanthogenate radical.)

No.	Composition of mixture. Na_2Bs.	KX.	KNO_3.	c_x.	*n*.
		$\mu = 0·6$.			
1	0·101	0·1	0·4	0·05	16·5
2	,,	0·2	0·3	0·15	25·0
3	,,	0·3	0·2	0·25	31·4
4	,,	0·4	0·1	0·35	34·8
5	,,	0·5	0·0	0·45	40·6
6	0·100	0·1	0·4	0·05	13·8
7	,,	0·2	0·3	0·15	21·6
8	,,	0·3	0·2	0·25	30·6
9	,,	0·4	0·1	0·35	37·8
10	,,	0·5	0·0	0·45	43·6
		$\mu = 2·3$.			
11	,,	0·5	1·5	0·45	48·9
12	,,	1·0	1·0	0·95	64·9
13	,,	1·5	0·5	1·45	70·8
14	,,	2·0	0·0	1·95	74·4

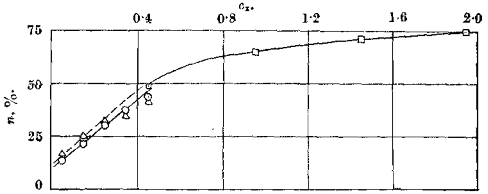
TABLE II.

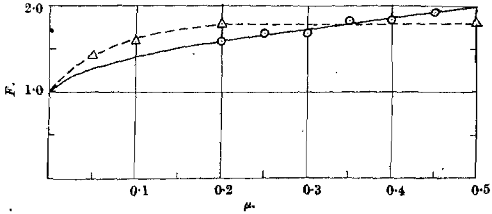
$Na_2Bs = 0·05$, $KX = 0·05$, $c_x = 0·025$.

No.	KNO_3 added.	μ.	n.	F.	No.	KNO_3 added.	μ.	n.	F.
15	0·00	0·20	5·78	1·60	18	0·15	0·35	6·64	1·84
16	0·05	0·25	6·13	1·70	19	0·20	0·40	6·68	1·85
17	0·10	0·30	6·13	1·70	20	0·25	0·45	6·97	1·93

FIG. 1.

△, ⊙, and ⊡ = values of n in Expts. 1–5, 6–10, and 11–14, respectively.





⊙ = values of F derived from experimental values of n.
△ „ „ „ calculated from solubility data.

FIG. 2.

have been found in Expts. 6—10 had the ionic strength here been 2·3, and so the curve for Expts. 11—14 is continued down to $c_x = 0·05$ as a broken line. Expts. 6—10 were a repetition of Expts. 1—5 but were carried out in a somewhat different manner, designed from the point of view of my conception of the reaction mechanism to ensure more definite results (see Experimental).

The values of F given in Table II and denoted by circles in Fig. 2 were obtained as follows: Since the results in Expts. 1—10 have shown that equation (1) is valid for the concentrations concerned, we are entitled to assume that the figures for n in Expts. 15—20 are proportional to the activity factor F in these experiments. If

these values of n are divided by 3·6 (found empirically) and the corresponding dividends are assigned to F, the curve obtained by plotting F against μ intersects the ordinate axis at $F = 1$, which is the theoretically correct value for the activity factor for $\mu = 0$, and hence these values of F were adopted.

For comparison, some values of the factor $F = f_1^2/f_2$ have been calculated from solubility experiments of Brönsted and Petersen (*J. Amer. Chem. Soc.*, 1921, **43**, 2274, 2282). The solubilities of *croceo*-tetranitrodiamminocobaltiate in salt solutions were used for the calculation of f_1, and those of *xantho*-oxalate for f_2. The values for F thus obtained are denoted by triangles in Fig. 2. It is seen that a common curve could be drawn to agree fairly well with all the points of the diagram, but the individual character of the two systems justifies different but similar curves.

EXPERIMENTAL.

Experiments 1—5 were carried out by dissolving a weighed quantity of *l*-bromosuccinic acid in the equivalent amount of sodium hydroxide solution, diluting it to a fixed volume, and adding solid potassium xanthogenate and solid potassium nitrate. Under these conditions, however, it is probable that some reaction takes place between the acid and the alkali before the addition of the xanthogenate, and in order to avoid this, the method was modified as follows: Weighed quantities of solid xanthogenate and nitrate were dissolved in an amount of sodium hydroxide solution equivalent to the quantity of *l*-bromosuccinic acid to be employed, and the solution was diluted to a fixed volume, and rapidly poured over the acid, which was brought into solution by vigorous shaking. The reaction mixture was then kept in the thermostat at 25·0° for about 72 hours, and the xanthogenosuccinic acid formed was isolated by acidification with sulphuric acid and extraction with ether. The ethereal solution was dried over calcium chloride and left to evaporate at room temperature. In most of the experiments xanthogenate was present in excess, and on acidification xanthogenic acid separated partly as a suspension and partly as a heavy oil; two or three filtrations through a wet filter-paper, however, sufficed to give a perfectly clear solution.

In the modified method of preparing the reaction mixture, the displacement of the bromine atom takes place in a solution in which the xanthogenate ion has the right concentration and the ionic strength is as required (except for the few moments necessary for dissolution of the acid); the corresponding experiments (Nos. 6—10) give a better curve than Nos. 1—5.

The xanthogenosuccinic acid thus obtained was yellowish-white

and crystalline, having a faint odour reminiscent of organic sulphides. It was not further purified for fear of fractionating it, and by titration with 0·1*N*-sodium hydroxide it gave an equivalent that agreed well with the theoretical value 119·1; hence, since Holmberg (*loc. cit.*) found the reaction to pursue a regular course, no further identification was thought necessary.

After being dried upon filter-paper, the acid was dissolved in ethyl acetate, and its rotation determined in 1-dcm. tubes surrounded by a jacket, through which water from a thermostat was circulated, the temperature being ascertained by a thermometer inserted in the solution itself. These measurements were made by the monochromatic light of the yellow mercury line ($\lambda = 578\ \mu\mu$), and in some special cases by the green mercury line ($\lambda = 546$) also, the light of a powerful mercury-quartz lamp being filtered through one of the two sets of aqueous solutions (1 cm. layer of each constituent solution):

A. Yellow line: (1) 5·76 g. of anhydrous copper sulphate in 100 c.c. of water; (2) 0·02 g. of tartrazine + 0·02 g. of erythrosin in 100 c.c. of water.

B. Green line: (1) the same as A1; (2) 18 g. of didymium chloride in 50 c.c. of water; (3) 0·02 g. of tartrazine in 100 c.c.

The *l*-bromosuccinic acid used was prepared from *l*-aspartic acid as described by Holmberg (*Ber.*, 1927, **60**, 2205). The sample used for Expts. 1—5 had $[\alpha]^{25°}_{578} = -74·67°$ ($c = 6·00$ in ethyl acetate), but that used in all the other experiments had $[\alpha]^{25°}_{578} = -73·84°$ under the same conditions. Since Walden (*Ber.*, 1895, **28**, 2770) found $[\alpha]_D = -72·6°$ and Holmberg (*Arkiv Kemi, Min., Geol.*, 1916, **2**, No. 8) found $[\alpha]^{17°}_D = -76·3°$, it is clear that the samples used here contained a few units % of the *r*-form, but as this would only cause a very slight uniform displacement of the curves, and in view of the small quantity available, it was decided not to recrystallise the acid.

The experimental details are given below.

Experiment 1. The quantities used were 3·006 g. of *l*-bromosuccinic acid, 2·404 g. of potassium xanthogenate (in the tables abbreviated to KX), 6·065 g. of potassium nitrate, and 30·75 c.c. of 1·0*N*-sodium hydroxide solution. Total volume, 150·0 c.c. The xanthogenosuccinic acid was extracted by four 50-c.c. portions of ether, whereby 3·09 g. were obtained: $[\alpha]^{25°}_{578} = -71·81°$ ($c = 6·03$ in ethyl acetate). The specific rotation of *l*-xanthogenosuccinic acid is estimated (see below) to be $[\alpha]^{25°}_{578} = -107°$; hence the content of *d*-form in the acid obtained in this experiment is calculated as $n = 16·45\%$.

In Expts. 2—5 the quantities of *l*-bromosuccinic acid and sodium hydroxide solution, the total volume, and the time of reaction (7

hours) were the same as in Expt. 1. The other quantities were as shown, and in every case the specific rotation refers to approximately 0·6 g. of acid in 10 c.c. of ethyl acetate (*i.e.*, $c = 6$).

Expt.	KX, g.	KNO_3, g.	Acid obtained, g.	$[\alpha]_{578}^{25°}$.	*n*, %.
2	4·808	4·549	3·10	—53·06°	25·00
3	7·212	3·033	3·02	—38·75	31·39
4	9·616	1·516	3·10	—32·48	34·83
5	12·020	—	3·32	—20·04	40·64

Expts. 6—10. 2·955 G. of *l*-bromosuccinic acid and 29·91 c.c. of sodium hydroxide solution (not the same as above) were used, the other conditions being the same as for Expts. 1—5.

6	2·405	6·066	3·34	—77·47*	13·80
7	4·809	4·550	3·24	—60·70*	21·64
8	7·214	3·033	—	—41·44*	30·64
9	9·618	1·517	—	—26·14*	37·74
10	12·023	—	—	—13·80*	43·55

* At 25·4°.

Expts. 11—14. The reaction product in these experiments was extracted successively with 100, 75, and 50 c.c. of ether; in all other respects the conditions were as in Expts. 6—10.

11	12·023	22·75	3·50	— 2·33	48·91
12	24·05	15·17	3·25	+31·79	64·86
13	36·07	7·583	—	+44·58†	70·84
14	48·09	—	—	+52·31‡	74·39

† $\alpha_{578}^{25°} = +2·67°$; $\alpha_{546}^{25°} = +3·11°$ ($c = 5·99$).

‡ At 25·2°; $[\alpha] = +53·31°$ at 20·9°.

From the observed rotations of Expt. 13, extrapolation shows that $[\alpha]_{580}^{25°}$ (*i.e.*, $[\alpha]_D^{25°}$) is 93% of the value of $[\alpha]_{578}^{25°}$; also the measurements in Expt. 14 show that a rise of 4·3° causes a decrease of 2% in α. From these and from Holmberg's value $[\alpha]_D^{20°} = \pm 101·5°$ for the pure xanthogenosuccinic acid, we can calculate that for this compound $[\alpha]_{578}^{25°} = \pm 107°$ (approx.), and this value has therefore been used in the present paper for the calculation of *n*.

Expts. 15—20. 1·478 G. of *l*-bromosuccinic acid, 1·202 g. of potassium xanthogenate, and 15·00 c.c. of sodium hydroxide solution were used in each case, the total volume being 150 c.c. The remaining data were:

Expt.	KNO_3, g.	Acid obtained, g.	$[\alpha]_{578}^{25·2°}$.	*n*, %.
15	—	1·63	—94·64°	5·78
16	0·758	1·63	—93·89	6·13
17	1·516	1·64	—93·89	6·13
18	2·275	1·62	—92·79	6·64
19	3·032	1·61	—92·70	6·68
20	3·790	1·64	—92·08	6·97

Polytechnic Institute,
Copenhagen, Denmark.

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LXVII.—*The Parachor and Chemical Constitution. Part XII. Fused Metals and Salts.*

By SAMUEL SUGDEN and HENRY WILKINS.

HE earlier papers of this series have been concerned chiefly with ıbstances which, in the liquid state, are non-conductors of elecricity; the parachors of conducting liquids (metals and salts) will ow be considered. These liquids exhibit many abnormalities in heir physical properties and are usually classed as highly associated ubstances (compare Turner, "Molecular Association," Longmans, reen, and Co., Ltd., 1915, pp. 27, 59). It is clear that the presence f a high concentration of charged ions or molecules must have a rofound effect upon the internal pressure of a liquid, for such harged particles possess a much larger external field of force than eutral molecules. It is therefore not surprising to find that the parachors of salts exhibit a number of anomalies and may be either greater or less than the predicted values. It will be clear from what follows that much more experimental work will have to be done before these anomalies can be accounted for satisfactorily. We are here making a preliminary survey of the field and intend to investigate more closely the types of substance in which anomalies have been encountered.

The parachor of a salt involves the constant for a polar bond. It has already been argued by one of us (Sugden, J., 1927, 1177) that this linkage should have the same effect upon the parachor as a semipolar double bond, *viz.*, $-1{\cdot}6$ units. A direct test of this hypothesis is provided by the parachors of certain salts of organic bases which are fusible without decomposition. For these substances all the atomic parachors involved are known with certainty and, from the work of Walden, Ulich, and Birr (*Z. physikal. Chem.*, 1928, **131**, 1, 21, 31), it is clear that fused salts of this type are highly dissociated into ions. The parachors of ten such salts are collected in Table I and are there compared with the parachors calculated on the assumption that the polar bond gives an increment of $-1{\cdot}6$ units. The first six substances in the table give parachors which, within the limits of experimental error, agree with the calculated values. The parachor of tetrapropylammonium picrate is of special interest, since Walden, Ulich, and Birr (*loc. cit.*) conclude that the picrates of quaternary bases are almost completely dissociated in the fused state. It is clear that the contribution of the polar bond to the parachor is very small and that the value $-1{\cdot}6$ for this constant can be regarded as satisfactory.

The six salts giving normal parachors are derived from secondary,

TABLE I.

Salts of Organic Bases.

Substance.	Observer.*	[P] obs.	[P] calc.	Diff.	k.
(1) Methylaniline hydrochloride	S. & W.	348·6	345·5	+ 3·1	2·11
(2) Ethylaniline hydrochloride	,,	381·9	384·5	— 2·6	2·08
(3) Dimethylammonium nitrate	W.	249·7	251·4	— 1·7	0·64
(4) Diethylammonium nitrate	,,	324·8	329·4	— 4·6	0·79
(5) Dimethylaniline bisulphate	S. & W.	469·5	472·3	— 2·8	1·28
(6) Tetrapropylammonium picrate ...	,,	931·8	928·3	+ 3·5	2·88
(7) Ethylammonium nitrate	,,	239·2	251·4	—12·2	0·47
,, ,, ...	W.	234·9	,,	—16·5	0·50
(8) Dimethylaniline hydrobromide ...	S. & W.	412·8	398·2	+14·6	1·06
,, ,, ...	W.	406·3	,,	+ 8·1	1·64
(9) Tri-*i*-amylammonium thiocyanate	,,	761·6	776·4	—14·8	1·48
(10) Tetra-*i*-amylammonium iodide ...	,,	895·5	950·3	—54·8	1·77

* For full references see p. 1296.

tertiary, and quaternary bases, and the first abnormal salt, No. 7, is the only salt of a primary base so far examined. A large specimen of this substance was prepared and purified by repeated freezing until its melting point became constant at 8°. Its purity was also confirmed by analysis, yet our measurements confirm the earlier results of Walden and show a parachor anomaly of —12 units. The behaviour of this substance is in striking contrast to that of the isomeric nitrate of dimethylamine, No. 3, which gives a normal parachor. A positive anomaly of the same order of magnitude (+ 15 units) is found for dimethylaniline hydrobromide (No. 8), whereas the bisulphate of the same base (No. 5) gives a nearly normal parachor. Walden's observations give large negative anomalies for the last two substances in the table; the very large deficit for No. 10 requires confirmation and may be due, in part, to the presence of a denser impurity.

Table I includes the value of the Ramsay–Shields coefficient, $k = d\gamma(M/D)^{2/3}/dT$, where the symbols have their usual significance. The molecular weight of the undissociated salt has been used to calculate the constant, yet none of the salts examined give a value of k approaching 3·5 which, on the usual interpretation of this constant, would correspond to complete dissociation into two ions. (The value 2·88 for tetrapropylammonium picrate is paralleled by values of k greater than 2·2 for many normal liquids of high molecular weight.) No connexion can be traced between the values of k and the occurrence of parachor anomalies; both normal and abnormal salts show a wide variation in the value of this coefficient.

The first two substances in Table I give $k = 2·1$, and in this respect might be regarded as normal (non-dissociated) liquids. We have therefore determined their electrical conductivity, with the results shown in Table II. These hydrochlorides are evidently

TABLE II.

Specific (κ) and Molecular (λ) Conductivities of Fused Salts of Organic Bases.

Methylaniline hydrochloride.			Ethylaniline hydrochloride.			Tetrapropylammonium picrate.			
t.	κ.	λ.	t.	κ.	λ.	t.	κ.	λ.	λη.
134°	0·0131	1·77	185°	0·0122	1·90	120°	0·0071	2·58	0·484
143·5	0·0156	2·12	197·5	0·0158	2·49	150	0·0140	5·19	0·453
155·5	0·0195	2·66	203·5	0·0176	2·77	180	0·0230	8·68	0·434
165·5	0·0259	3·55	209·5	0·0195	3·09	210	0·0327	12·57	0·411

largely ionised in the liquid state and have conductivities comparable with those of the fused picrates studied by Walden, Ulich, and Birr (*loc. cit.*). Some of the data of these workers on tetrapropylammonium picrate are included in Table II for comparison. For this substance, as for other salts of quaternary bases, the product of molecular conductivity and viscosity (λη) diminishes slowly with rising temperature and has approximately the same value as is found for the same salt in dilute aqueous solution, *viz.*, 0·486. It must therefore be almost completely dissociated into ions in the fused state.

A discussion of the parachors of the salts of inorganic bases involves first of all a knowledge of the atomic constant for the metal. These constants are known with fair accuracy from measurements on covalent compounds of mercury (68·7), thallium (65·5), aluminium (38·6), tin (56·5), lead (76·2), and antimony (66·0). Table III gives the parachors of a number of salts of these elements and also those of the free metals. The latter are assumed to be monatomic and the polar bond in the salts is assigned the value −1·6. Some of the experimental data are open to criticism; in particular Smith's data for the surface tension of the metals are often not confirmed by later workers.

It will be seen that the parachors of these metals and salts frequently exhibit large positive anomalies. In many cases these are too large to be accounted for by association of two or more atoms or ions to give a complex linked by multiple bonds. For instance, if two thallous ions unite to give a complex ion (I), containing a double bond, the parachor increment per thallium atom is 23·2/2 = 11·6, whereas the anomaly found in the nitrate is nearly twice this quantity. Similarly for metallic tin it is necessary to assume the

Tl=Tl	Sn≣Sn	=Sn=Sn=Sn=
$\Delta P = 11·6$	$\Delta P = 23·2$	$\Delta P = 23·2$
(I.)	(II.)	(III.)

improbable structure (II), in which two tin atoms are linked by a quadruple bond and share eight electrons, or the equally improbable

TABLE III.

Fused Metals and Inorganic Salts.

Substance.	Observer.	[P] obs.	[P] calc.	Diff.
Thallous formate	S.	150·3	145·8	+ 4·5
,, acetate	,,	183·5	184·4	— 0·9
,, nitrate	,,	177·3	158·0	+19·3
,, ,, ...	J.	180·7	,,	+22·7
Stannous chloride	,,	183·8	165·1	+18·7
Lead chloride	L. & K.	194·5	184·8	+ 9·7
Mercury	Smith	68·0	68·7	— 0·7
,, ...	H. & E.	69·0	,,	+ 0·3
,, ...	H	69·4	,,	+ 0·7
,, ...	Br.	69·4	,,	+ 0·7
Aluminium	Smith	55·0	38·6	+16·4
Tin	,,	83·4	56·5	+26·9
,, ...	Bi.	83·8	,,	+27·3
,, ...	S. & D.	86·8	,,	+30·3
Lead	Smith	114·2	76·2	+38·0
,, ...	H.	89·3	,,	+13·1
,, ...	Bi.	91·5	,,	+15·3
,, ...	D. & S.	93·5	,,	+17·3
Antimony	Smith	76·8	66·0	+10·8
,, ...	Bi.	82·0	,,	+16·0
,, ...	D. & S.	83·9	,,	+17·9

structure (III), containing chains of tin atoms linked by double bonds, in order to account approximately for the parachor anomalies. It is more probable that some other factor has to be taken into account due either to the presence of a high concentration of ions or of loosely bound electrons, or else to some special condition of the metallic atom. In this connexion it should be noted that Sidgwick ("The Electronic Theory of Valency," Clarendon Press, 1927, pp. 179—181) has directed attention to the remarkable chemical inertness of a pair of electrons in the atoms of certain elements, *e.g.*, thallium, tin, lead, and antimony, all of which exhibit positive parachor anomalies. In many compounds this pair of electrons behaves as if it were part of the core and could not be removed by ionisation.

Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) has measured the surface tensions and densities of a number of salts of the alkali metals. The parachors calculated from these observations are summarised in Table IV and are used to obtain approximate atomic parachors for the metallic elements. Jaeger's surface tensions often cover a much wider range than his density measurements; to avoid errors of extrapolation the parachors have been calculated only for the range of temperatures covered by the density observations. This range is indicated in the second column and the variation in parachor over this range is given in the third column. The fifth column gives the parachor of the anion + the constant for a polar bond; by subtracting this from the mean parachor of the salt, the constant for the metal is obtained.

TABLE IV.

Salts of the Alkali Metals.

Substance.	Temperature.	Parachor.	Mean [P].	Σ[P].	Atomic parachor.
LiF	850—1000°	57·8— 59·3	58·5	24·1	34·4
LiCl	600— 775	97·2— 99·6	98·4	52·7	45·7
$LiNO_3$ ...	350— 500	130·0—132·9	131·5	91·5	40·0
Li_2SO_4 ...	860—1150	212·4—220·6	216·0	121·8	47·1 × 2
NaF	1010—1190	81·5— 83·9	82·7	24·1	58·6
NaCl	800— 900	123·4—126·7	124·8	52·7	72·1
NaBr ...	760— 900	142·2—145·4	143·8	66·4	77·4
NaI	700— 750	169·4—171·3	170·8	89·4	81·4
$NaNO_3$ ...	320— 600	147·9—158·4	152·9	91·5	61·4
$NaPO_3$ ...	800—1100	175·4—181·7	178·1	117·7	60·4
Na_2SO_4 ...	900—1100	257·5—265·8	261·1	121·8	69·6 × 2
KF	900—1100	106·7—111·0	109·0	24·1	84·9
KCl	800— 900	154·6—158·4	156·6	52·7	103·9
KBr	775— 825	173·6—175·1	174·3	66·4	107·9
KI	737— 812	204·3—206·8	205·2	89·4	115·8
KNO_3 ...	380— 580	184·2—193·6	189·0	91·5	97·5
KPO_3 ...	900—1200	201·4—207·0	204·4	117·7	86·7
K_2SO_4 ...	1070—1350	319·5—336·5	328·0	121·8	103·1 × 2
RbF	800—1040	121·2—125·9	123·1	24·1	99·0
RbCl	750— 880	181·0—185·0	182·8	52·7	130·1
RbBr ...	730— 830	190·5—195·0	192·7	66·4	126·3
RbI	670— 820	224·3—229·5	226·8	89·4	137·4
$RbNO_3$ ...	320— 580	192·5—203·7	197·9	91·5	106·4
Rb_2SO_4 ...	1080—1350	356·9—368·1	361·8	121·8	120·0 × 2
CsF	720— 880	135·4—138·6	136·9	24·1	112·8
CsCl	660— 770	186·6—190·7	188·7	52·7	136·0
CsBr	650— 770	205·2—209·2	207·5	66·4	141·1
CsI	650— 770	239·8—245·0	242·4	89·4	153·0
$CsNO_3$ ...	425— 575	215·7—221·2	218·0	91·5	126·5
Cs_2SO_4 ...	1030—1220	386·8—393·1	388·8	121·8	133·5 × 2

Approximate atomic parachors: Li = 50, Na = 80, K = 110, Rb = 130, Cs = 150.

From a survey of the data in Table IV it will be seen that the bromides and iodides usually give the highest values for the metallic parachors and the sulphates, nitrates, phosphates, and particularly the fluorides give much lower figures. At present the only other evidence for the parachors of these elements is furnished by the determination of the surface tension of metallic sodium by Poindexter (*Physical Rev.*, 1926, **27**, 820), from which Na = 97·4. This is much larger than the highest value deduced from the salts. It must be remembered, however, that this figure refers to a neutral sodium atom with an electron in the M level, whereas the constant deduced from the salts refers to a sodium ion in which this level is unoccupied. It is hoped shortly to obtain the parachors of co-ordinated compounds of the alkali metals, *e.g.*, with β-diketones, which should give further information as to their atomic parachors. Meanwhile the figures given at the bottom of Table IV may be taken as rough minimum values.

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EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); and densities by means of the U-shaped pyknometer previously described (J., 1924, **125**, 1171), except for the more hygroscopic salts, for which calibrated floats were used in sealed tubes. The parachor is calculated by the formula $[P] = M\gamma^{1/4}/D$, where M is the molecular weight, γ the surface tension in dynes/cm., and D the density of the liquid.

Methylaniline hydrochloride, $C_7H_{10}NCl$, $M = 143{\cdot}6$, was prepared by passing dry hydrogen chloride into a ligroin solution of the base and was recrystallised from benzene–chloroform. The specimen used melted at 122·5—123° (corr.) after thorough drying in a vacuum desiccator. Densities determined (floats): $D_{4^\circ}^{128\cdot5^\circ}$ 1·0660, $D_{4^\circ}^{143^\circ}$ 1·0590, $D_{4^\circ}^{149\cdot5^\circ}$ 1·0557, $D_{4^\circ}^{167\cdot5^\circ}$ 1·0447; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}0808 - 0{\cdot}000527\,(t - 100)$.

t	130°	140·5°	150·5°	160°	
γ	44·53	43·50	42·68	41·29	
D	1·0634	1·0564	1·0517	1·0462	
$[P]$	348·7	348·9	348·8	347·7	Mean 348·5

Ethylaniline hydrochloride, $C_8H_{12}NCl$, $M = 157{\cdot}6$, was prepared by dissolving the base (100 g.) in concentrated hydrochloric acid (70 c.c.). On cooling, the salt crystallised. The base was regenerated and again crystallised as hydrochloride. A little reddish colouring matter was removed by washing with absolute alcohol, and the product thoroughly dried; m. p. 178·5° (corr.). Densities determined (floats): $D_{4^\circ}^{182\cdot5^\circ}$ 1·0085, $D_{4^\circ}^{203^\circ}$ 0·9984; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}0492 - 0{\cdot}000493\,(t - 100)$. Above 200° the substance decomposed with evolution of gas.

t	173·5°	180·5°	188·5°	
γ	35·82	35·41	34·50	
D	1·0098	1·0061	1·0019	
$[P]$	382·0	382·3	381·4	Mean 381·9

Tetrapropylammonium picrate, $C_{18}H_{30}O_7N_4$, $M = 414·3$. The bromide was first prepared and recrystallised from ethyl acetate until pure, m. p. 252° (corr.) (Found: Br, 29·66. Calc.: Br, 30·03%). This was converted into the picrate, which melted at 117·5—118° (corr.). Densities determined: $D_{4°}^{125·5°}$ 1·136, $D_{4°}^{141·5°}$ 1·122, $D_{4°}^{149°}$ 1·115; whence $D_{4°}^{t°} = 1·159 - 0·00086(t - 100)$. These figures are in good agreement with the densities found by Walden, Ulich, and Birr (*loc. cit.*).

t	129°	135°	143·5°	152·5°	
γ	41·80	41·30	40·72	40·03	
D	1·134	1·129	1·122	1·114	
$[P]$	929·0	929·9	932·6	935·6	Mean 931·8

Ethylamine nitrate, $C_2H_8O_3N_2$, $M = 108·1$, was prepared by dissolving a slight excess of the base in 20% nitric acid and removing the water under diminished pressure. The residual oil was frozen and the crystals were collected in a chilled funnel. This process was repeated until a constant melting point of 8° (corr.) was attained [Found: HNO_3 (by nitron), 59·1, 59·25. Calc.: HNO_3, 58·3%]. Densities determined: $D_{4°}^{12°}$ 1·216, $D_{4°}^{32°}$ 1·199, $D_{4°}^{55°}$ 1·182, $D_{4°}^{70°}$ 1·168; whence $D_{4°}^{t°} = 1·225 - 0·00080\ t$.

t	11°	30°	56·5°	82·5°	97°	
γ	48·8	47·6	46·2	45·4	44·9	
D	1·216	1·201	1·180	1·159	1·148	
$[P]$	235·0	236·5	238·8	242·1	243·8	Mean 239·2

Dimethylaniline hydrobromide, $C_8H_{12}NBr$, $M = 202·0$, was prepared by dissolving the base in a slight excess of constant-boiling hydrobromic acid and removing the water under diminished pressure. The solid product was purified by precipitation from solution in dry chloroform by the addition of ethyl acetate. The specimen used melted at 84·5—85·5° (corr.) (Found: Br, 39·5. Calc.: Br, 39·6%). Densities determined: $D_{4°}^{110·5°}$ 1·302, $D_{4°}^{120°}$ 1·294, $D_{4°}^{130°}$ 1·286, $D_{4°}^{141·5°}$ 1·277; whence $D_{4°}^{t°} = 1·398 - 0·00864\ t$.

t	97°	112°	118·5°	129°	136·5°	
γ	50·40	49·55	49·00	48·60	48·07	
D	1·314	1·301	1·296	1·287	1·280	
$[P]$	409·7	412·1	412·3	414·4	415·7	Mean 412·8

Dimethylaniline bisulphate, $C_8H_{13}O_4NS$, $M = 219·2$, was prepared by dissolving the calculated amount of the base in 50% sulphuric acid and removing the water under diminished pressure. It was purified by solution in dry chloroform and precipitation at 0° by addition of ethyl acetate; m. p. 88—89° (corr.) (Found: SO_4, 43·1. Calc.: SO_4, 43·8%). Densities determined: $D_{4°}^{114·5°}$ 1·272, $D_{4°}^{120°}$ 1·268, $D_{4°}^{129·5°}$ 1·260, $D_{4°}^{137°}$ 1·256; whence $D_{4°}^{t°} = 1·283 - 0·00074\ (t - 100)$.

t	105·5°	114·5°	126°	133°	
γ	55·2	54·9	54·0	53·7	
D	1·279	1·272	1·264	1·259	
$[P]$	467·1	469·0	470·0	471·3	Mean 469·5

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, April 24th*, 1929.]

CLXVIII.—*The Parachor and Chemical Constitution. Part XIII. Some Compounds of Titanium and Tin.*

By FREDERICK BASIL GARNER and SAMUEL SUGDEN.

THE chief object of the investigation described below was the elucidation of the structure of the additive compound of stannic chloride and phosphorus oxychloride described by Casselman (*Annalen*, 1854, **91**, 242; 1856, **98**, 217). As a preliminary step it was necessary to measure the parachors of a few simple tin compounds in order to determine the atomic parachor of this element. The results in Table I (which includes the parachor of titanium tetrachloride) give for the atomic constants Sn = 56·7 and Ti = 45·3.

TABLE I.

Atomic Parachors of Tin and Titanium.

Substance.	$[P]$ obs.	$\Sigma[P]$.	Atomic parachor.
Tin tetrachloride	272·8	217·2	55·6
Tin tetrabromide	325·8	272·0	53·8
Tin tetraethyl	441·1	380·4	60·7
			Mean 56·7
Titanium tetrachloride	262·5	217·2	45·3

These values are in harmony with those of other elements of group IV which have so far been determined and give the sequence :—

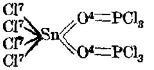
C.	Si.	Ti.	Ge.	Zr.	Sn.	Hf.	Pb.
2·8	*ca.* 25	45·3	—	—	56·7	—	76·4

The compound of stannic chloride and phosphorus oxychloride is formed at once with considerable evolution of heat when the components are mixed in suitable proportion. Casselman (*loc. cit.*) describes it as melting at 55° and boiling at 180°, and gives its composition as $SnCl_4,POCl_3$. We have been unable to isolate a compound of this composition and boiling point but from all the mix-

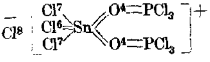
tures used have obtained a substance which, after careful purification, melts at 54·5° (corr.) and boils at 118—119° (corr.)/760 mm. On analysis this substance was found to have the formula $SnCl_4,2POCl_3$ and thus falls into line with the corresponding compounds of zirconium and hafnium, namely, $Zr(Hf)Cl_4,2POCl_3$, and $Zr(Hf)Cl_4,2PCl_5$. The analytical results are shown below.

	Calculated for		Found.	
	$SnCl_4,POCl_3$.	$SnCl_4,2POCl_3$.	I.	II.
Sn	28·68%	20·92%	21·00%	21·20%
P	7·49	10·92	10·62	10·97
Cl	59·98	62·60	—	62·10

The structure suggested for this substance by one of us (Sugden, J., 1927, 1182), when modified to account for the presence of two phosphorus oxychloride molecules in the complex, is shown by formula (I) and contains four singlet linkages. The parachor calculated for this structure is 665·5, whereas the value found experimentally is 691·6, which is 26 units too high. This result may be



[P] calc., 665·5.
(I.)



[P] calc., 688·7.
(II.)

accounted for in two ways. In the first place the substance distils with some decomposition at ordinary pressure and the first runnings always contain an excess of stannic chloride. It is therefore possible that, in the liquid state, the compound is partly dissociated into its generators, so that only a portion of it has the structure (I). It may be noted here that, if the octet rule holds and the substance has an open-chain non-polar structure, then at least four singlet linkages must be present in the molecule. This can be proved in the following manner: The total number of valency electrons in the molecule is 96. If the 15 atoms in the molecule all attain an octet, the number of shared electrons is $8 \times 15 - 96 = 24$. The minimum number of bonds which will link the 15 atoms to form a non-polar molecule is 14, so that the 24 shared electrons must be distributed between 10 duplet links and 4 singlets. The introduction of double bonds or ring structures necessitates the use of a still larger number of singlets in order to provide the necessary number of bonds.

If, however, the substance has a polar structure, the number of bonds required is smaller and the presence of a smaller number of singlet linkages can be admitted. For instance, if one of the

chlorine atoms ionises to give the structure (II), only two singlets are necessary to formulate the complex kation and the calculated parachor (688·7) is very nearly equal to the experimental value. This polar structure is, however, difficult to reconcile with the properties of the substance, *viz.*, its fusibility, volatility, and solubility in hydrocarbon solvents. We therefore measured the conductivity of the compound in the fused state, with the results shown below. As the absorption of moisture gives ionisable products, care was taken to expose the substance as little as possible to the atmosphere. Specimen I was recrystallised from ligroin and showed a small conductivity. Specimen II was purified by distillation under diminished pressure and was stored in sealed tubes. After melting, the tube was opened and the contents were rapidly transferred to the stoppered conductivity cell. A much

Specimen.	Specific conductivity at 60°.
I	0·00136 mho
II	0·000081 ,,
II + $\frac{1}{4}$% water	0·00132 ,,

smaller conductivity was found for this specimen, and, after addition of $\frac{1}{4}$% of water, the conductivity showed a large increase. A 4% solution of the substance in benzene was also examined and had no measurable conductivity ($<10^{-6}$ mho). We conclude that the small conductivity shown by the fused substance is due to traces of moisture and that the molecule must be non-polar. Its structure is probably represented by (I), but the parachor shows that it is largely dissociated into its generators in the liquid state.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, 1922, **121**, 858; 1924, **125**, 27), and densities with a U-shaped pyknometer (J., 1924, **125**, 1171). Since most of the substances studied are rapidly hydrolysed by moisture, long tubes containing phosphoric oxide were used to dry the air entering the bubbler or pyknometer.

The tables below are set out in the same manner as in other papers of this series and do not need further description. The parachor is calculated by the formula $[P] = \gamma^{\frac{1}{4}} M/(D - d)$, where γ is the surface tension in dynes/cm., M the molecular weight, and D and d the densities of the liquid and vapour respectively. For the substances studied in the present paper, d is very small and has been neglected.

Stannic chloride, $SnCl_4$, $M = 260·5$, was purified by distillation and had b. p. 114° (corr.)/768 mm. Densities determined: $D_{4°}^{t°}$

2·220, $D^{27·5°}_{4°}$ 2·194, $D^{46°}_{4°}$ 2·169, $D^{55·5°}_{4°}$ 2·152; whence $D^{t°}_{4°} = 2·284 - 0·00239t$.

t	12°	29·5°	40°	51°	58·5°	
γ	31·15	29·01	27·39	26·63	25·02	
D	2·255	2·213	2·188	2·162	2·144	
[P] ...	272·9	273·2	272·4	273·7	271·7	Mean 272·8

Stannic bromide, $SnBr_4$, $M = 438·5$, was purified by distillation and had m. p. 29·5° (corr.) and b. p. 204° (corr.)/765 mm. Densities determined: $D^{37·5°}_{4°}$ 3·320, $D^{51·5°}_{4°}$ 3·282, $D^{61°}_{4°}$ 3·253, $D^{71°}_{4°}$ 3·225, $D^{81·5°}_{4°}$ 3·197; whence $D^{t°}_{4°} = 3·427 - 0·00284\,t$.

t	37°	51·5°	64°	75·5°	
γ	37·76	35·32	33·91	32·09	
D	3·322	3·281	3·246	3·212	
[P]	326·3	325·8	326·0	325·1	Mean 325·8

Tin tetraethyl, $Sn(C_2H_5)_4$, $M = 234·9$, was prepared by the action of excess of magnesium ethyl bromide on stannic bromide (Pfeiffer and Schnurmann, *Ber.*, 1904, 37, 320) and was purified by distillation. The specimen used had b. p. 180·5—181·5° (corr.)/768 mm. Densities determined: $D^{15°}_{4°}$ 1·202, $D^{28·5°}_{4°}$ 1·187, $D^{40·5°}_{4°}$ 1·172, $D^{52°}_{4°}$ 1·160, $D^{64°}_{4°}$ 1·147; whence $D^{t°}_{4°} = 1·219 - 0·00113\,t$.

t	13·5°	34·5°	46°	55·5°	77·5°	
γ	26·22	24·05	22·98	22·08	20·41	
D	1·204	1·180	1·167	1·156	1·131	
[P] ...	441·6	440·9	440·8	440·6	441·4	Mean 441·1

Additive compound of stannic chloride and phosphorus oxychloride, $SnCl_4,2POCl_3$, $M = 567·3$. When stannic chloride (1 mol.) and phosphorus oxychloride (2 mols.) are mixed, considerable heat is evolved; on cooling, the mixture solidifies completely. Three methods of purification were attempted. The crude substance was melted and after partial solidification the crystals were separated and drained. Owing to the ready absorption of moisture the melting point could not be raised above 52·5° by this method. By crystallisation from ligroin the pure substance was obtained melting about 2° higher, but the crystals were frequently discoloured or turned brown on keeping. Distillation at atmospheric pressure gave a boiling point of 118—119°, but some decomposition occurred and the first runnings did not solidify completely. The best method of purification was found to be distillation at about 100 mm. pressure. Three distillation flasks with long necks (to minimise contact of the vapours with the rubber bungs) were connected in series and thoroughly dried by heating with a flame in a current of dry air. The compound was introduced into the first flask, and the system connected to the pump through a guard tube containing calcium chloride. The substance readily distilled at 70°/100 mm.

and in one distillation was obtained pure with m. p. 54·5° (corr.). This was unchanged by further distillation or by sublimation in a sealed tube at room temperature.

Analysis. Tin was estimated by precipitation as sulphide and was weighed as oxide. The phosphorus was estimated as magnesium pyrophosphate, and the chloride as silver chloride. The analytical figures are given on p. 1299.

An attempt was made to prepare the substance described by Casselman (*loc. cit.*) by mixing equimolecular quantities of the components. The product, on distillation, gave a first fraction, b. p. 114°, which was chiefly stannic chloride, and a later fraction which partly solidified and on further distillation gave the compound described above. Densities determined : $D_{4°}^{56·5°}$ 1·923, $D_{4°}^{62·5°}$ 1·907, $D_{4°}^{67·5°}$ 1·892 ; whence $D_{4°}^{t°} = 2·090 - 0·00293\,t$.

t	57·5°	64°	67·5°	71·5°	74°	81·5°
γ	29·88	29·12	28·27	27·70	27·27	25·87
D	1·922	1·903	1·893	1·880	1·873	1·851
$[P]$	690·2	693·3	690·8	692·1	692·1	691·1
						Mean 691·6

Titanium tetrachloride, $TiCl_4$, $M = 189·9$. A commercial specimen was purified by distillation ; the fraction used was pale yellow and had b. p. 136°/753 mm. Densities determined : $D_{4°}^{15·5°}$ 1·742, $D_{4°}^{26°}$ 1·725, $D_{4°}^{40°}$ 1·701, $D_{4°}^{58·5°}$ 1·673 ; whence $D_{4°}^{t°} = 1·767 - 0·00162\,t$.

t	13°	27·5°	39·5°	52°	75°	
γ	34·03	32·16	30·78	29·08	26·65	
D	1·746	1·722	1·703	1·683	1·645	
$[P]$ ...	262·8	262·6	262·7	262·0	262·3	Mean 262·5

We wish to acknowledge the help of Mr. A. Skinner in the preliminary work. One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, May 7th, 1929.*]

CLXIX.—*The Effect of a Gas upon the Pressure of a Vapour.*

By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

THE work of Regnault (*Ann. Chim. Phys.*, 1845, **15**, 129 ; *Mem. Acad. Sci.*, 1862, **26**, 679) and others shows quite conclusively that the pressure of a saturated vapour in equilibrium with its liquid is lowered by the presence of an indifferent gas. Campbell (*Trans.*

Faraday Soc., 1915, **10**, 197), in particular, in a study of the saturated vapour pressures of eight different liquids in contact with air, hydrogen, and carbon dioxide, observed and measured this effect and showed that in certain cases it attained a considerable magnitude, the vapour pressures of chloroform and methyl alcohol in an atmosphere of carbon dioxide, for example, being only about three-quarters of the values in the absence of the gas.

It follows that the concentration of a saturated vapour in a gas is *not a true measure of the vapour pressure of the liquid* and, therefore, that the very large number of "vapour pressure" measurements which have been made by the gas-saturation method are subject to an error, unknown in extent but, in some cases at least, of very considerable magnitude.

Campbell advanced the theory that the low values he obtained were due to the adsorption of gas at the liquid–gas interface, and we have sought, in the work now reported, to apply a crucial test of the validity of his view, according to which, evidently, in the absence of liquid a gas should have no effect on the pressure of a vapour. We have therefore measured independently both the concentration and the pressure of a vapour in the presence and in the absence of a gas, the gas used being carbon dioxide and the vapour either (1) ether or (2) pentane. It seems rather remarkable that, though many *so-called measurements of vapour pressure (being in fact measurements of vapour concentration in a gas)* have given results differing in a systematic fashion from those of true vapour-pressure measurements in the absence of gases, there is no recorded case of the precise measurement simultaneously of the pressure and the concentration of a vapour. Admittedly the experimental difficulties of such measurements are considerable, but the results are likely to be of great interest.

The method here described is so laborious as to be unsuitable for the investigation of a large number of cases. Attempts are therefore being made to develop a simpler and more speedy technique without substantial loss of accuracy. Meanwhile the present results are recorded, as they appear definitely to contradict the view that the diminution of vapour pressure of a liquid in presence of a gas can be wholly attributed to the effects of solution or adsorption of gas in the liquid.

EXPERIMENTAL.

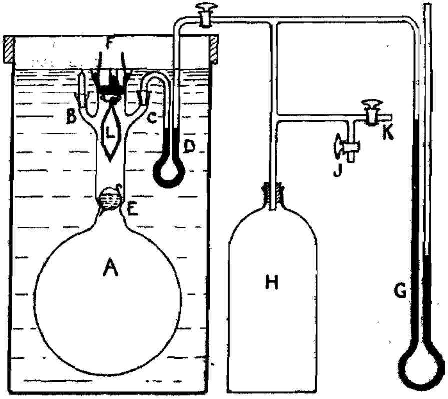
The ether used was prepared from a specially good commercial sample, supplied by Messrs. McFarlane, by repeated fractional distillation from metallic sodium after standing for some months over solid caustic potash and potassium permanganate. Carbon

dioxide was prepared from marble in a Kipp's apparatus, well washed, and dried over phosphoric oxide.

To determine the concentration : pressure ratio for ether, precisely known weights of the liquid were taken in evacuated sealed glass bulbs, these were broken in a glass flask of known volume, previously either evacuated or filled with carbon dioxide at a known pressure, and the resulting pressure change was measured.

Thin-walled glass bulbs having a capacity of 3—10 c.c. were charged with various quantities of ether by the method of Briscoe

FIG. 1.



and Little (J., 1914, **105**, 1326). Each bulb was weighed against a tare to 0·01 mg. before and after filling and sealing, a correction being applied for the weight of air excluded from the bulb when finally weighed.

The apparatus used is shown diagrammatically in Fig. 1. A flask, A, of about 1200 c.c. capacity, had the neck indented at E to support the bulbs and was closed by a mercury-sealed ground glass stopper F. The stopper carried two sealed-in platinum wire loops, from which a chisel-ended glass hammer, L, was suspended by means of a bridge of tin fuse-wire. By connecting the platinum leads to a 6-volt accumulator the tin wire suspension could be fused

at will, thus releasing the hammer, which smashed the bulb and (if all went well) was itself held by the indentations.

Two side tubes carrying mercury-sealed ground joints were provided: B was used for evacuation or introduction of gas, and C was connected through the mercury-filled isoteniscope, D, to a large bottle, H, and the manometer G. The pressure in H could be regulated with nicety by evacuation at J or admission of air at K. The flask and isoteniscope were immersed in a large glass-sided thermostat maintained electrically at 25·00° $\pm$ 0·002° and a microscope was used to observe equality of pressure on the two sides of the isoteniscope, the cross-wire being set upon the images of the menisci while both sides were open to the atmosphere. The pressure in H, when shown in this way to be equal to that in A, was observed, by means of a good cathetometer reading to 0·02 mm., on the manometer, G, the limbs of which were made of 9 mm. internal diameter in order to minimise capillary errors.

In determining unsaturated vapour pressures in the absence of gas, the flask was first thoroughly evacuated through B and this tube was sealed off. Then the pressure in H was reduced until the levels of mercury in the isoteniscope D were exactly equal, and the pressure was read on the manometer. The bulb was then broken and when, after the lapse of 3—4 hours, the pressure in A had become constant, the pressure in H was again adjusted to precise equality with that in A and read on the manometer.

The difference in the manometer readings, corrected to 0°, then measured the unsaturated vapour pressure due to a known weight of ether contained in a space given by the internal volume of the flask and side tubes *less* the volumes of the hammer and the broken glass of the bulb. The gross internal volume of the flask was ascertained by weighing it filled with water in the usual way.

Determinations of unsaturated vapour pressures in the presence of carbon dioxide were made in a similar way, except that the flask was first filled with carbon dioxide at a pressure of approximately 500 mm., which was accurately read after it had attained a constant value. Then the bulb of ether was broken as before and, after the pressure had become constant (8—10 hours), the pressure in the flask was again read. In cases where the pressure within the flask was greater than that of the atmosphere, compressed air was introduced through the tap K. The observed rise in pressure within the flask was slightly less than the true pressure exerted by the ether vapour, because when the bulb was broken the carbon dioxide had increased in volume by an amount equal to the internal volume of the bulb. Thus, in a typical case :—

Pressure of CO_2 before breaking of bulb = 495·58 mm. Hg.
Internal volume of bulb = 3·28 c.c.
Final total volume of CO_2 + ether vapour = 1208·89 c.c.
Pressure of CO_2 alone in the volume occupied by ether vapour
and $CO_2 = 495{\cdot}58 \times \frac{1208{\cdot}89 - 3{\cdot}28}{1208{\cdot}89} = 494{\cdot}24$ mm. Hg.

Stress is laid upon the necessity for this correction, because it appears to have been overlooked by Campbell (*loc. cit.*) in his application of a method similar in principle to that now described.

The experiments with pentane were performed in a precisely similar manner to those with ether. The pentane was a pure sample supplied by Messrs. Kahlbaum.

	No.	Corrected net volume of flask (c.c.).	Initial pressure (mm. Hg at 0°).	Final pressure (mm. Hg at 0°).	Vapour pressure (mm. Hg at 0°).	Weight of vapour (g.).	Vapour pressure of 1 g. vapour per litre.
Ether in vacuum	1	1208·30	1·82	44·87	43·05	0·20374	255·3
	2	1208·54	0·38	106·81	106·43	0·51787	247·8
	3	1208·97	0·56	108·38	107·82	0·52624	247·7
	4	1208·62	0·76	173·11	172·35	0·83987	248·0
	5	1208·47	0·31	243·39	243·08	1·18576	247·7
	6	1208·53	0·50	445·01	444·51	2·20679	243·4
Ether in carbon dioxide	7	1208·89	*494·24	537·07	42·83	0·20552	251·9
	8	1208·36	*499·81	710·46	210·65	1·04588	243·4
	9	1208·48	*497·21	757·19	259·98	1·29962	241·8
Pentane in vacuum	10	1205·96	0·05	137·51	137·46	0·65710	252·3
	11	1205·98	0·05	368·79	368·74	1·78672	248·9
	12	1208·46	0·12	534·31	534·19	2·48909	259·4
	13	1206·09	2·54	520·28	517·74	2·52863	247·0
Pentane in carbon dioxide	14	1206·25	*497·14	782·47	285·33	1·48577	231·7
	15	1206·31	*497·70	954·47	456·77	2·27006	242·7

* Corrected for internal volume of weighing bulb.

The results of these experiments are shown in the above table and, although in the case of ether they are less consistent than was to be expected from the precautions taken, yet they show a definite lowering of the unsaturated vapour pressure in the presence of carbon dioxide at a pressure of approximately 50 cm. of mercury. The effects of adsorption of ether upon the walls of the flask are very evident in that the unsaturated vapour pressure exerted by 1 g. of vapour in 1 litre of space diminishes progressively as the actual concentration of vapour increases. In this connexion it should be noted that the flask received the same treatment before each determination; it was scoured with a solution of chromic and

nitric acids, washed thoroughly with pure water, alcohol and ether, and dried by passing through it a current of pure air.

In comparing the unsaturated vapour pressures in a vacuum with those in carbon dioxide it is necessary, therefore, to consider corresponding vapour concentrations. Thus, if the results here recorded are plotted on a graph, the lowering of unsaturated vapour pressure on the basis of 1 g. of vapour per litre will be seen to vary from a minimum of 3·4 mm. to a maximum of approximately 5·9 mm. of mercury for ether in carbon dioxide at a pressure of approximately 50 cm. of mercury.

In the case of pentane there is a grave irregularity in the results obtained which is difficult to understand. It would appear, however, that the lowering of the unsaturated vapour pressure of pentane in presence of carbon dioxide is distinctly greater than the corresponding lowering of unsaturated vapour pressure of ether, but the results are put forward merely as indicating a general tendency.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, March 28th, 1929.*]

CLXX.—*Studies in Complex Salts. Part II. The Preparation, Properties and Stability of Some Bis-dicarboxylato Copper Salts.*

By HARRY LISTER RILEY.

IT has been suggested (J., 1928, 2985) that an important factor governing the formation of a co-ordinate linkage between two ions is the distribution of the electric charges in the donor ion. If it were possible to compare the stabilities of a series of complex ions of the type $[AX_1]$, $[AX_2]$, $[AX_3]$, etc., in which A represents the same acceptor ion and X_1, X_2, X_3, etc., represent different donor ions, valuable information would be obtained as to the electron distribution in this series of ions. A survey of complex-salt chemistry indicated that such a comparison would present many difficulties, chiefly in the choice of a suitable series of complex ions, definitely recognised as such, the stabilities of which could be measured; for those acceptor ions which form the largest numbers of complex ions are those which easily pass from one state of valency to another and therefore render any measurements of ion concentration by an electrode potential or conductivity method uncertain. It appeared possible, however, that a series of such measurements might be possible in the case of copper complex salts. The

complex-salt chemistry of copper was subjected to extended investigation by Pickering (J., 1911—1915) with reference to its compounds with hydroxy-substituted carboxylic and dicarboxylic acids, but no attempt was made to correlate the compounds obtained with the co-ordination theory. It was therefore decided to investigate the nature of the compounds obtained when copper reacts in aqueous solution with certain dicarboxylic acids in order to determine whether or no a suitable series of similar complex copper salts could be obtained. The carboxylic acids chosen for this study were carbonic, oxalic, malonic, succinic, and phthalic.

The nature of the double compound formed between copper carbonate and sodium carbonate has been studied by Reynolds (J., 1898, **73**, 262), Gröger (*Ber.*, 1901, **34**, 429), Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 171), Pickering (J., 1909, **95**, 1418; 1911, **99**, 800), Applebey and Lane (J., 1918, **113**, 610), Aldridge and Applebey (J., 1922, **121**, 242), and de Carli and Agostini (*Atti R. Accad. Lincei*, 1928, **7**, 921). The weight of evidence appears to be in favour of the formation of the compound $Na_2CO_3,CuCO_3,3H_2O$ and de Carli and Agostini have recently shown (*loc. cit.*) that one molecule of water is lost at 80° and the other two molecules at 120°. It would therefore seem correct on the co-ordination theory to formulate this compound as

$$Na_2[Cu(CO_3)_2(H_2O)_2],H_2O$$

or as $Na_2[Cu(CO_3)_2(H_2O)_3]$, in which one of the carbonato-groups occupies only one position in the co-ordinated complex. The double oxalate of lithium and copper was first prepared by Troost (*Ann. Chim. Phys.*, 1857, **51**, 143), who described it as a compound which forms sky-blue needles and has the formula

$$Li_2C_2O_4,CuC_2O_4,2H_2O.$$

No further study of the double oxalates appears to have been made. It has now been shown that the double *sodium copper* salt also crystallises in sky-blue needles which are readily soluble in water. The two molecules of water are not lost when the salt is kept in a vacuum. It is therefore probably best formulated as $Na_2[Cu(C_2O_4)_2(H_2O)_2]$. Malonic acid forms a similar *compound*, $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$, which is a pale blue, sparingly soluble powder, and phthalic acid also forms a *compound* of the same type, $Na_2[Cu(C_8H_4O_4)_2(H_2O)_2]$, which is easily decomposed by water and is of a deep blue colour. Although none of these compounds has yet been resolved, it seems highly probable that the two molecules of water are co-ordinated with the copper, as they are not removed by desiccation in a vacuum and, what is perhaps more important, they occur in each of these four compounds. The copper ion is therefore apparently displaying a co-ordination number of six.

This view is supported by the work of Wahl (*Soc. Sci. Fennicae, Comm. Phys. Math.*, 1927, **4**, 1), who has resolved a compound very similar in type to the above, *viz.*, diethylenediaminediaquocupric tartrate.

The literature contains few references to the double alkali copper succinates. Reynolds (J., 1898, **73**, 701) describes a compound of the formula $CuK_4(C_4H_4O_4)_3,2H_2O$ and Pickering (J., 1911, **99**, 800) reports $K_2Cu(C_4H_4O_4)_2$. The succinato- and the carbonato-compounds are, however, extremely unstable, existing in aqueous solution only in presence of a very large excess of alkali succinate and carbonate respectively, and it was therefore decided to confine the quantitative measurements of stability to the oxalato-, malonato-, and phthalato-compounds. It seems, however, fairly certain that the carbonato- and succinato-compounds are of the same type, though considerably less stable than the others. In order to form some idea of the relative stabilities of the carbonato- and succinato-compounds the following experiment was performed. Some freshly etched copper was immersed for several weeks in a concentrated solution of sodium carbonate in an open flask. The intensity of the blue colour produced was compared with that formed in a solution of sodium succinate of similar strength, also containing a piece of copper. In the carbonate solution quite a deep blue colour was produced, whereas in the succinate solution only a very pale blue colour was formed; thus showing that the carbonato-ion has a greater tendency than the succinato-ion to co-ordinate with the copper.

Preparation of Disodium Diaquodioxalatocupriate.—26·8 G. of pure sodium oxalate were dissolved in 800 c.c. of water and to the hot solution was added a concentrated solution of copper sulphate until a very faint turbidity was produced. This was cleared by the addition of a little more sodium oxalate solution and the resulting deep blue solution was filtered and allowed to crystallise. The *dioxalato*-compound separated in long, sky-blue needles, which were collected and washed with cold water until free from sulphate and then with alcohol and with ether. After drying in the air, the compound was analysed. The oxalate was estimated by direct titration with standard permanganate in hot acid solution. The copper was weighed as cuprous sulphide, and the sodium as sodium sulphate after separation of the copper with hydrogen sulphide (Found: C_2O_4, 54·51; Cu, 19·89; Na, 14·32. $Na_2[Cu(C_2O_4)_2(H_2O)_2]$ requires C_2O_4, 54·73; Cu, 19·77; Na, 14·30%). No loss in weight occurred over concentrated sulphuric acid in a vacuum. The compound is fairly readily soluble in cold water, giving a deep blue solution; this is only slightly decomposed by prolonged boiling, but

a precipitate of copper oxalate is produced at once on the addition of dilute hydrochloric acid. Calcium chloride gives a precipitate of calcium oxalate when added to the cold solution.

Preparation of Disodium Diaquodimalonatocupriate.—To 33·2 g. of sodium malonate, dissolved in 150 c.c. of water, were added 25 g. of copper sulphate, dissolved in 100 c.c. of water. The deep blue solution produced was filtered quickly; on standing, it deposited the *dimalonato*-compound as a pale blue powder. This was collected, washed with cold water until free from sulphate and then with alcohol and with ether. After drying on a porous plate, the compound was analysed, copper and sodium being estimated as before and carbon and hydrogen by combustion (Found: Cu, 18·16; Na, 13·12; C, 20·63; H, 2·36. $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$ requires Cu, 18·19; Na, 13·16; C, 20·60; H, 2·29%). No loss in weight occurred on drying in a vacuum. The malonato-compound is paler in colour than the oxalato and somewhat less soluble in water.

Preparation of Disodium Diphthalatodiaquocupriate.—To a solution of 33·2 g. of phthalic acid in the equivalent quantity of aqueous sodium hydroxide were added 200 c.c. of 0·2*M*-copper sulphate (10 g. of $CuSO_4,5H_2O$). The large excess of phthalate was used in order to diminish hydrolysis. From the deep blue, filtered solution, nothing separated over-night, but on vigorous stirring the *diphthalato-compound* was precipitated in blue flakes, deeper in colour than the oxalato-compound. The diphthalato-compound apparently possesses the property of forming highly supersaturated solutions. The separated solid was dried by thorough pressing between filter-papers; it could not be washed, even with a cold 50% alcohol–water mixture, such treatment causing hydrolysis. The dried compound was free from sulphate (Found: Na, 9·81; Cu, 13·46; C, 40·59; H, 2·62. $Na_2[Cu(C_8H_4O_4)_2(H_2O)_2]$ requires Na, 9·71; Cu, 13·42; C, 40·54; H, 2·53%). Practically theoretical yields were obtained in each case.

The constants of instability of these three compounds (*i.e.*, $[Cu^{++}][X^{--}]^2/[CuX_2^{--}]$, where X = the carboxylato-ion) were measured by an electrode potential method, the following concentration cell being used: Cu|0·01*M*-$CuSO_4$|Sat. KNO_3|0·01*M*-$CuSO_4$ + 0·03*M*-Na_2X|Cu, where Na_2X represents the sodium salt of the dicarboxylic acid under consideration. Preliminary investigation showed that 0·03*M*-solutions of the dicarboxylic acid were most suitable for these measurements for two reasons; *viz.*, the excess of free dicarboxylate being reduced to a minimum (the phthalato-compound just giving a clear solution under these conditions), the solvent action of the dicarboxylate on the copper

electrode, in presence of traces of oxygen, will also be reduced to a minimum; and secondly, the uncombined dicarboxylate may, in the calculation of the instability constant, be assumed, without any appreciable error being introduced, to be completely dissociated. The following assumptions were made in calculating the constants of instability: (1) $[Cu^{++}]$ is given by the expression $E = RT/nF \cdot \log C_2/C_1$; (2) the concentration of the undissociated complex ion present can be calculated from "total copper present minus $[Cu^{++}]$"; (3) the concentration of the free dicarboxylato-ion is equal to the total dicarboxylate present ($0{\cdot}03M$) less that united to the undissociated copper.

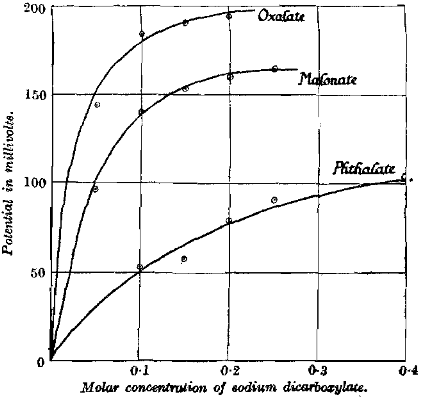
The potential measurements were made by means of a metre bridge potentiometer, a capillary electrometer, and a standard Weston cell. The half-elements were small wide-mouthed glass bottles, of about 40 c.c. capacity, each carrying a rubber bung through which passed a piece of stout copper wire (S.W.G. 14) and the usual glass tubes. Four such half-elements were constructed and the copper electrodes, after being etched in dilute nitric acid, were washed, connected together, and plated (current density, 0·5 amp. per 100 sq. cm.) in a bath of the following composition: $CuSO_4,5H_2O$, 30 g.; H_2SO_4, 10 g.; alcohol, 50 g.; water, 200 g. The plating was continued for 48 hours, the circuit was then broken, and the electrodes, still connected together, were left in the plating solution for a further period of 3 days. They were then removed, rapidly rinsed with cold, air-free, distilled water, dried, and introduced at once into their respective half-element cells.

The solutions used in the half-elements were made up from a standard solution of copper sulphate ($0{\cdot}1M$) and standard solutions of the sodium salts of the respective dicarboxylic acids ($0{\cdot}12M$). In the standard sodium oxalate solution, "reagent" sodium oxalate, previously dried at 110°, was used. For the malonate and phthalate solutions the pure recrystallised acids were neutralised by the exactly equivalent quantities of carbonate-free, standard caustic soda, and the solutions made up to a definite volume. Before the copper sulphate solution was mixed with the solution of the sodium dicarboxylate, both solutions were boiled, to remove dissolved air, rapidly cooled, and made up to a definite volume with air-free, distilled water. The half-elements were completely filled with their respective solutions and tightly stoppered. By these means the amount of dissolved oxygen in the various solutions was reduced to a minimum.

Some preliminary measurements indicating the variation of the potential of the concentration cells with the concentration of the sodium dicarboxylate are shown in Fig. 1. These results were

obtained with 0·02*M*-copper sulphate. Fig. 2 shows the variation of potential with time in cells containing 0·01*M*-copper sulphate and 0·03*M*-sodium dicarboxylate. The potentials were measured against the same 0·01*M*-copper sulphate half-element. The potentials fell rapidly at first and then became steady after a few hours. The effect of admitting oxygen (at point A) is shown in the oxalate curve, a slow but steady fall resulting. This effect is not so marked with the malonate and the phthalate. The values obtained are reproducible to within 1 or 2 millivolts. All the measurements were carried out at room temperature.

Fig. 1.



The values obtained for the constants of instability were as follows :—

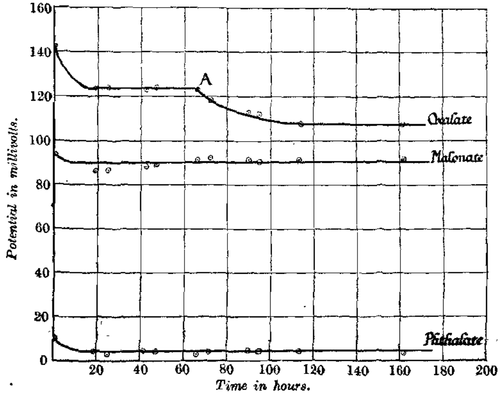
Compound.	Potential (volt).	$[Cu^{++}]$.	$[X^{--}]$.	$[CuX_2^{--}]$.	$\frac{[Cu^{++}][X^{--}]^2}{[CuX_2^{--}]}$
Oxalato......	0·124	$0·33 \times 10^{-4}$	0·0100	0·0100	$0·33 \times 10^{-6}$
Malonato ...	0·089	$0·54 \times 10^{-5}$	0·0100	0·0100	$0·54 \times 10^{-7}$
Phthalato...	0·004	$0·46 \times 10^{-2}$	0·0192	0·0054	$0·31 \times 10^{-4}$

The concentration of the copper ions in 0·01*M*-copper sulphate at 18° is taken to be $0·629 \times 10^{-2}$ (see Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475).

The instability constant of the phthalato-compound cannot be considered strictly accurate owing to the comparatively high con-

centration of the copper ions. These experiments show, however, that the stabilities of the complex ions formed between copper and the various dicarboxylic acids are in the following decreasing order of stability: oxalato, malonato, phthalato, carbonato, and succinato. The chelate rings formed in the various ions would be $>Cu<{}^{O}_{O}>CO$, $>Cu<{}^{O\cdot CO}_{O\cdot CO}$, etc. The phthalato-compound is unique amongst complex salts in possessing two seven-membered chelate rings.

FIG. 2.



At first sight it appears that the cause of this gradation of stability is the strain in the chelate ring and that the effects observed can be explained by purely steric considerations, the magnitude of the charge on the oxygen atom taking part in the Cu—O bond being a minor consideration. It will be shown, however, in Part III of this series that strain, as a purely steric effect, is totally inadequate to account for the stability of certain substituted malonic acid complex salts and that the chief factor governing stability must be a polar one. It would be premature, however, to theorise as to the polar factors which govern the stability of the complex salts studied in this paper, as the chelate rings concerned contain different numbers of atoms and it is impossible to discriminate between strain and polar factors.

Summary.

Copper forms with certain dicarboxylic acids complex salts of the type $Na_2[Cu(X)_2(H_2O)_2]$ in which the copper is probably displaying a co-ordination number of six.

The preparation of the dioxalato-, the dimalonato-, and the diphthalato-complex salts has been described.

The stabilities of the complexes formed have been shown to be in the following decreasing order: oxalato, malonato, phthalato, carbonato, and succinato.

The author wishes to express his thanks to Dr. H. J. T. Ellingham for the loan of apparatus and for advice on the measurement of the electrode potentials.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, March 28th*, 1929.]

CLXXI.—*Nicotine Tetrachloroiodide.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

THE authors have shown (J., 1924, **125**, 183, 1980) that many organic bases form stable tetrachloroiodides, those of the simpler nitrogen bases and of diazonium salts having been described. As might be expected, similar derivatives of many alkaloids can be prepared, among which the tetrachloroiodide of nicotine presents features of interest, since no other equally well-crystallised derivative of nicotine is known.

Nicotine tetrachloroiodide separates quantitatively when a solution of the base in hydrochloric acid is added to a similar solution of iodine trichloride. Since nicotine is a di-tertiary base, one molecule combines with two equivalents of tetrachloroiodic acid and the compound has the constitution $C_{10}H_{14}N_2,2HICl_4$.

Nicotine tetrachloroiodide is a very stable substance; it can be kept without alteration for an indefinite period in an ordinary corked specimen tube, and does not lose weight when exposed for a considerable period in a vacuum desiccator over lime. It is decomposed by aqueous alkalis, and more slowly by water alone, giving mainly a mixture of free nicotine and nicotinic acid, together with iodate and iodide.

The preparation of pure nicotine free from the small quantities of related alkaloids and other substances with which it is associated in the tobacco plant has hitherto presented considerable difficulty.

The tetrachloroiodide affords a ready means of effecting this separation, since it can be obtained from the crude material in a state of purity with very little loss by recrystallisation from glacial acetic acid. On decomposing the pure tetrachloroiodide with sodium sulphite and making the solution alkaline with potash, pure nicotine is liberated, and can be extracted with ether.

Well-crystallised *tetrachloroiodides* are also yielded by nicotinic acid (I), methyl *N*-methylnicotinate (II), and trigonelline (nicotinic acid methyl betaine) (III).

$CO_2H{\cdot}C_5H_4N{\cdot}HICl_4$	$CO_2Me{\cdot}C_5H_4NMe{\cdot}ICl_4$	$CO_2H{\cdot}C_5H_4NMe{\cdot}ICl_4$
(I.)	(II.)	(III.)

Experimental.

Nicotine Tetrachloroiodide.—Ten g. of pure nicotine, dissolved in 20 c.c. of cooled concentrated hydrochloric acid, were added to a solution of iodine trichloride prepared by saturating a suspension of 8 g. of iodine in 100 c.c. of concentrated hydrochloric acid with chlorine. A thick yellow precipitate at once separated. A slow stream of chlorine was passed through the mixture for a short time. The precipitate was then filtered off, washed with a little concentrated hydrochloric acid, and recrystallised from hot glacial acetic acid containing a little iodine trichloride, a slow stream of chlorine being passed through the solution during cooling; *nicotine tetrachloroiodide* separated in very beautiful, orange prisms, m. p. 150° (decomp.) (Found: Cl, 40·7; I, 35·8. $C_{10}H_{16}N_2Cl_8I_2$ requires Cl, 40·5; I, 36·1%).

Nicotinic Acid Tetrachloroiodide.—To a solution of 10 g. of nicotinic acid in 150 c.c. of concentrated hydrochloric acid, 20 g. of powdered iodine were added. Chlorine was then passed until the whole was saturated. *Nicotinic acid tetrachloroiodide* separated as a bright yellow precipitate. This was filtered off and recrystallised from a mixture of equal parts of concentrated hydrochloric acid and glacial acetic acid to which a little iodine trichloride had been added, small yellow needles, m. p. 137°, very slowly separating (yield, 30 g. Theoretical yield, 31·5 g.) (Found: Cl, 36·35. $C_6H_5O_2N,HICl_4$ requires Cl, 36·1%).

Nicotinic acid tetrachloroiodide is insoluble in water and concentrated hydrochloric acid. It is decomposed by aqueous sodium sulphite, nicotinic acid being re-formed.

Methyl N-*methylnicotinate tetrachloroiodide*, prepared similarly, crystallises from hot glacial acetic acid, containing a little iodine trichloride, in bright yellow needles, m. p. 110° (Found: Cl, 33·6. $C_8H_{10}O_2NCl_4I$ requires Cl, 33·7%).

Trigonelline similarly forms a *tetrachloroiodide*, which crystallises from a mixture of glacial acetic acid and hydrochloric acid, to which a little iodine trichloride has been added, in small, bright yellow prisms, m. p. 122° (Found: Cl, 34·7. $C_7H_8O_2NCl_4I$ requires Cl, 34·9%).

Decomposition of Nicotine Tetrachloroiodide by Sodium Sulphite.—Nicotine tetrachloroiodide (50 g.), suspended in 80 c.c. of water and cooled to 0°, was added *gradually, with constant stirring, to a cooled* solution of 40 g. of sodium sulphite in 200 c.c. of water. Sodium hydroxide (40 g., dissolved in 100 c.c. of water) was then added, and the whole extracted four times with ether. After the extract had been dried with anhydrous potassium carbonate, and the ether evaporated, the residue was distilled in a current of hydrogen, 10 g. of pure nicotine, b. p. 249—250°, being obtained (yield, 90%).

Preparation of Pure Nicotine Tetrachloroiodide from Technical Nicotine.—Two recrystallisations from glacial acetic acid were found sufficient to free the crude nicotine tetrachloroiodide from the tetrachloroiodides of the other bases present in technical nicotine.

100 G. of commercial nicotine were dissolved in 200 c.c. of concentrated hydrochloric acid and added to a solution of iodine trichloride obtained by passing excess of chlorine through a suspension of 80 g. of iodine in 400 c.c. of concentrated hydrochloric acid. The thick yellow precipitate which separated was twice recrystallised from 750 c.c. of hot glacial acetic acid (containing a little iodine trichloride), 372 g. of pure nicotine tetrachloroiodide, m. p. 150°, being obtained.

Isolation of Pure Nicotine from Tobacco.—Two hundred g. of dried, powdered tobacco (dark rag tobacco) were ground with a solution of 80 g. of sodium hydroxide in 1000 c.c. of water and steam-distilled. The bulk of the nicotine came over in the first 1400 c.c. and when 1800 c.c. had been collected, no nicotine could be detected in the distillate. The aqueous distillate was cooled, saturated with hydrogen chloride, and a solution of iodine trichloride in hydrochloric acid (*containing 12 g. of iodine*) was added. The thick yellow precipitate which separated was filtered off and twice recrystallised from 50 c.c. of glacial acetic acid containing a little iodine trichloride, 22 g. of pure nicotine tetrachloroiodide being obtained. This, when decomposed with 10 g. of sodium sulphite and extracted as described above, yielded 4·5 g. of pure nicotine.

Decomposition of Nicotine Tetrachloroiodide by Caustic Alkalis.—Ten g. of nicotine tetrachloroiodide were added gradually to a cooled solution of 4 g. of sodium hydroxide in 50 c.c. of water. Much heat was developed and a small quantity of tarry matter separated, which was filtered off. The filtrate was extracted re-

peatedly with ether. On evaporation of the ether, 1·5 g. of nicotine were obtained. The aqueous liquid from which the nicotine had been extracted was then made acid with hydrochloric acid and evaporated to dryness, and the residue extracted with a little concentrated hydrochloric acid. The acid extract was added to excess of a solution of tetrachloroiodic acid; 1·7 g. of nicotinic acid tetrachloroiodide then separated as a bright yellow solid.

Ten g. of nicotine tetrachloride thus yielded nicotine and nicotinic acid corresponding to 6·75 g. and 3·16 g., *i.e.*, to 99% of the tetrachloroiodide used.

THE QUEEN'S COLLEGE, OXFORD. [*Received, April 6th*, 1929.]

CLXXII.—*New Polynuclear Co-ordination Compounds of Cobalt.*

By EDMUND GEORGE VINCENT PERCIVAL and WILLIAM WARDLAW.

THE polynuclear metal-ammines have, in many cases, somewhat complex empirical formulæ, but by the application of simple rules their probable configurations can be deduced.

Werner assigned an octahedral distribution to the units associated with the central cobalt, chromium, or platinum atom and demonstrated that it was possible to link such octahedra at one, two or three points by suitable bridge atoms or groups. He specially emphasised that in such polynuclear complexes the metallic atoms are never directly linked with one another.

Werner explained that an OH or NH_2 group was able to link two cobalt atoms because the oxygen or nitrogen atom possessed both principal and auxiliary valency. The electronic theory of valency, however, presents a clearer explanation of why these and similar groups can act as linkages in the same way as O, O_2, SO_4, C_2O_4, NH. In the latter type of linkage the metal atoms form non-polar single bonds with the associating unit, whilst the other linkages are connected by one non-polar bond and one co-ordinate link.

The exact structure of salts containing the O_2 linkage is still unsettled. For such a linkage the structures $\underset{\overset{\downarrow}{O}}{\mathrm{Co{-}O{-}Co}}$ and Co–O–O–Co are both possible. A real difficulty arises, however, when an attempt is made to assign a suitable configuration to the product formed by the oxidation of such a compound as

$$[(NH_3)_5Co{-}O_2{-}Co(NH_3)_5]X_4.$$

The dark green substance obtained is stated by Werner to contain

the oxygen molecule in a much more stable condition than before the oxidation, and he formulates the new product as

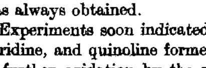
$$[(NH_3)_5Co^{III}-O_2-Co^{IV}(NH_3)_5]X_5.$$

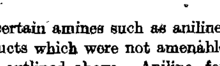
This formulation postulates the co-existence of ter- and quadrivalent cobalt and has been employed by Werner to give a suitable configuration to a large number of polynuclear cobalt ammines ("Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," 1920 ed., pp. 293 *et seq.*).

A more satisfactory explanation is difficult to find in spite of the fact that such a formulation means, in the special case mentioned above, that two atoms of cobalt with effective atomic numbers of 36 form a less stable association with an oxygen molecule than one atom of effective atomic number 35 and another of effective atomic number 36.

Nevertheless Werner concluded from an investigation of a large range of metal-ammines that the maximum co-ordination number of the cobalt was 6 irrespective of whether the metal was ter- or quadrivalent.

It was this conclusion that led Bucknall and Wardlaw (*J.*, 1928, 2648) to reinvestigate the reaction which takes place when dry air is drawn through an alcoholic solution of cobaltous chloride containing allylamine. As a result they concluded that the product obtained was *not* $[2O_2Co6R]Cl_3,H_2O_2$, containing cobalt with a co-ordination number of 8 as previously described by Pieroni (*Gazzetta*, 1921, **51**, i, 42), but a polynuclear complex of the probable configuration (I; R = CH_2:CH·CH_2·NH_2), where the cobalt has valencies of 3 and 4 and a co-ordination number of 6.


(I.)


(II.)

In view of the isolation of this compound from a non-aqueous solvent it seemed of interest to determine whether the reaction was typical of amines generally and whether the same type of product was always obtained.

Experiments soon indicated that certain amines such as aniline, pyridine, and quinoline formed products which were not amenable to further oxidation by the method outlined above. Aniline, for example, gave an insoluble blue compound of the composition $CoCl_2,2C_6H_5·NH_2$ which on recrystallisation from alcohol yielded the red substance $CoCl_2,2C_6H_5·NH_2,2C_2H_5·OH$ (Lippmann and Vortmann, *Ber.*, 1878, **11**, 1069). It seems highly probable that in this case there is formed the very stable co-ordination compound

[$CoCl_2$·$2C_6H_5(NH_2)$·$2C_2H_5(OH)$], which is unaffected by atmospheric oxygen.

Of a large number of amines investigated, satisfactory results were only recorded in the case of propylamine and benzylamine and the reaction with allylamine was confirmed. With ethylamine the reaction appeared to follow a similar course, but the yield of product was insufficient for complete analysis. It is not without significance that each amine contains the group CH_2·NH_2, *viz.*, CH_2:CH·CH_2·NH_2, C_2H_5·CH_2·NH_2 and C_6H_5·CH_2·NH_2.

In all cases the amine occupies one position in the co-ordination sphere; the products from the reaction with allylamine and propylamine have the general formula (I), and the product from benzylamine the formula (II).

In formula (I) both ter- and quadri-valent cobalt atoms are present, whereas in (II) both cobalt atoms are tervalent. Cobalt exhibits throughout a co-ordination number of 6.

EXPERIMENTAL.

The ethyl alcohol used in the following experiments was dried by refluxing and distilling it twice over barium oxide and twice over calcium turnings. The amines were purchased samples dried by two distillations over sodium.

The red compound (I; R = CH_2:CH·CH_2·NH_2) produced by the oxidation of a mixture of cobaltous chloride (dried at 140°) in dry alcohol in the presence of dry allylamine (Bucknall and Wardlaw, *loc. cit.*) has again been prepared and analysed (Found: Co, 18·5; Cl, 16·7; C, 33·7; H, 7·1; N, 13·5. Calc.: Co, 18·6; Cl, 16·8; C, 34·1; H, 7·0; N, 13·3%).

Hexa-allylamineperoxodihydroxodicobalt Trinitrate (formula as I).—To a solution (40 c.c.) of the complex chloride (2 g.) in water, pure nitric acid (1 c.c.) was added. The pink precipitate produced was washed free from acid with water and dried in a vacuum over calcium chloride (Found: Co, 16·6; N, 17·6. $C_{18}H_{44}O_{13}N_9Co_2$ requires Co, 16·6; N, 17·7%).

These results confirm those set out in the previous communication and disprove the formula proposed by Pieroni (*loc. cit.*) for the complex chloride.

Hexapropylamineperoxodihydroxodicobalt Trichloride (I; R = Pr^{α}·NH_2).—To a saturated solution of cobalt chloride (dried at 140°) in dry alcohol (75 c.c.), dry *n*-propylamine (20 c.c.) was added in small quantities with constant shaking. Considerable heat was evolved and a bluish-red solution resulted, from which, however, no addition compound separated even on cooling in a freezing mixture (compare cobalt allylamines). The mixture was oxidised for about

30 hours by means of a slow stream of air, washed and dried by passage through soda lime tubes and sulphuric acid bubblers. The red crystalline precipitate which separated was washed with dry alcohol and dried in a vacuum over calcium chloride.

Cobalt was estimated as sulphate by ignition of the substance with sulphuric and nitric acids in an air-bath, gradually raised to about 410°. Chlorine was estimated as silver chloride after removal of cobalt as hydroxide on the addition of sodium hydroxide to a solution of the substance (Found: Co, 18·5; Cl, 16·6; C, 33·2; H, 8·6; N, 13·1. $C_{18}H_{56}O_4N_6Cl_3Co_2$ requires Co, 18·3; Cl, 16·5; C, 33·5; H, 8·7; N, 13·0%).

The complex chloride is very soluble in water, giving a neutral solution, and the addition of nitric acid produces, as in the case of the allylamine complex, an insoluble nitrate, all the chlorine having been displaced. Heated to 70°, an aqueous solution of the salt yields brown cobalt hydroxide and propylamine is liberated. Ammonium sulphide immediately precipitates cobalt as sulphide. Concentrated hydrochloric acid gives a green solution. The complex salt liberates iodine from potassium iodide solution on warming.

Molecular-weight determinations. The molecular weight of the complex chloride was determined by the depression of the freezing point of water. If the above formula is correct, four ions should be present in solution and the apparent molecular weight should be about 160 when ionisation is complete. The results furnish evidence in favour of this formulation:

G. of substance per *100 g. water.*	Conc. (mols. per *1000 g. water*).	Osmotic *factor.*	Apparent *mol. wt.*
1·251	0·01941	3·32	194
1·634	0·02536	3·13	205
1·822	0·02827	3·12	206

Molecular-conductivity determinations. The molecular conductivity of the complex chloride was found for various dilutions at 0°:

v (litres/mol.)	35·4	70·8	141·6	283·2	566·4
μ	94·7	108·4	132·0	140·0	145·0

The values of the molecular conductivities of two typical salts at 0° are given for comparison:

v (litres/mol.)	32	64	128	256	512	1024
$K_4Fe(CN)_6$	215	227	243	254	264	282
$K_4W(CN)_8$	211	224	238	250	259	264

From the results for the complex chloride, μ_∞ is estimated to be about 180. The values of μ, as in the case of the corresponding allylamine derivative, are less than would be expected for a normal

four-ion compound. They are, however, in accordance with the formula if it is assumed, as is probably the case, that the large complex ion is slow-moving.

Hexabenzylaminetrihydroxodicobalt Trichloride (II; $R' = C_6H_5{\cdot}CH_2{\cdot}NH_2$).—To a saturated solution of cobaltous chloride (20 g., dried at 140°) in 200 c.c. of dry alcohol, dry benzylamine (25 g.) was added slowly with shaking; a white precipitate separated. The mixture was oxidised for about 150 hours by a slow current of air, dried and purified as previously described. The purple-red crystalline product was washed with alcohol and dried in a vacuum over calcium chloride (Found: Co, 12·7; Cl, 11·6; C, 54·2; H, 6·2; N, 9·2. $C_{42}H_{57}O_3N_6Cl_3Co_2$ requires Co, 12·9; Cl, 11·6; C, 54·9; H, 6·2; N, 9·2%).

The complex salt is very similar in colour to purpureo-cobaltic chloride, and is insoluble in water and alcohol, physico-chemical measurements thus being precluded. A suspension in water decomposed on being heated to 70°, with formation of cobalt hydroxide and the liberation of benzylamine and benzaldehyde. Cold concentrated nitric acid did not form a nitrate as in the two previous cases. Iodine was not liberated from potassium iodide solution by this salt (unlike the peroxo-compounds) on warming in the presence of acetic acid.

Oxidation of Cobaltous Chloride in Alcohol in the Presence of Other Amines.—Ethylamine. On the addition of the amine a violet solution was obtained which yielded on oxidation a red liquor, from which a small quantity of solid separated. The yields, however, were always very small.

Ethylenediamine. The amine was thoroughly dried over sodium. Many experiments were carried out, but the brown product isolated was of variable composition. It was, however, capable of recrystallisation from aqueous alcohol and the chief product after this treatment was triethylenediaminecobaltic chloride,

$$[Co3\,en]Cl_3,3H_2O;$$

a small quantity of a red compound was also isolated. The above complex salt was also obtained when ethylenediamine was oxidised in aqueous solution in the presence of cobaltous chloride.

Methylamine, diethylamine, and piperidine. These bases always gave greenish precipitates, however thoroughly the drying process was carried out. In no case was the characteristic red oxidised solution produced.

It is evident that oxidation of cobaltous chloride in alcohol in the presence of amines does not always produce polynuclear complexes. So far, only primary amines containing the $CH_2{\cdot}NH_2$ group have been satisfactory for this purpose.

The authors wish to express their thanks for the award of a Priestley Scholarship to one of them (E. G. V. P.). They are also indebted to the Chemical Society for a grant in aid of this investigation.

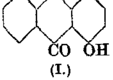
UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, April* 18*th*, 1929.]

CLXXIII.—1-*Methoxy-derivatives of Thioxanthone.*

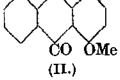
By KENNETH CHARLES ROBERTS and SAMUEL SMILES.

IT has been shown (this vol., p. 863) that the basic character of the thioxanthone nucleus as indicated by the stability of the salts is promoted by the presence of methoxyl; this influence does not primarily depend on the number of methoxyl groups but rather on their position. The influence of the 1-methoxyl group is remarkable, the salts formed from 1-methoxy-thioxanthones having characteristic physical properties and being more stable than those yielded by other methoxy-derivatives. Further evidence of this distinctive effect of 1-methoxyl has now been obtained.

When *p*-methoxyphenol is treated in the usual manner with 2-thiolbenzoic acid, the two possible hydroxymethoxythioxanthones (I and II) are formed. One of these gave a characteristic *diacetoborate*, from which the original material was regenerated by hydrolysis; this substance must therefore be (Dimroth, *Annalen*, 1926, **446**, 97) the 1-*hydroxy*-4-*methoxy*-derivative (I). The isomeride was thus evidently the 4-*hydroxy*-1-*methoxythioxanthone* (II), and accordingly it did not yield a diacetoborate but was merely acetylated by the boroacetic anhydride; also it was easily converted by aqueous alkaline methylation into 1 : 4-dimethoxythioxanthone.



(I.)



(II.)

$$\left[S{<}{}^{C_6H_4}_{C_6H_4}{>}C{:}O{\rightarrow}H\right]X$$

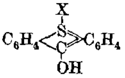
(III.)

The separation of the two substances was readily effected by hydrochloric acid or by aqueous alkali hydroxide, in both of which the 4-hydroxy-1-methoxy-derivative is soluble. The insolubility of 1-hydroxy-4-methoxythioxanthone in aqueous alkali is noteworthy. The basic character of these isomerides was examined by the methods previously described (*loc. cit.*, p. 867). The results, which are collected below, together with data from the 1 : 4-dihydroxy- and dimethoxy-thioxanthones for comparison,

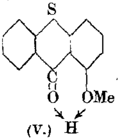
how the distinctive effect of the 1-methoxyl group and amplify the vidence previously adduced.

Derivative.	Mols. HCl added.	Colour of salts.	Titration (c.c.).
-Hydroxy-1-methoxy	2	crimson	28
-Hydroxy-4-methoxy	none	—	6
: 4-Dihydroxy	none	—	4—5
: 4-Dimethoxy	2	crimson	28

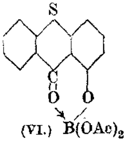
In expressing the structure of the salts of thioxanthone and its lerivatives the views of Pfeiffer ("Organische Molekulverbindungen," Stuttgart, p. 192) on the character of salts and additive products of ketones have been adopted. These lead in the first instance to the formulation (III); expressions involving the *o*-quinonoid (IV) or the corresponding quinocarbonium structures have been avoided, since the salts in question are difficult to reduce and do not exhibit the characteristics usually associated with such systems. The distinctive effect of the 1-methoxyl group on the stability and physical character of the salts is readily explained by the assumption that in these hydrogen, exerting the dicovalence for which Sidgwick (" Electronic Theory of Valency," 1927, p. 72; J., 1924, **125**, 532; also Werner, " Neuere Anschauungen," 1913, p. 259) has adduced ample evidence, plays the part of a chelate member of a ring system (V).



(IV.)

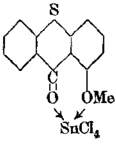


(V.)



(VI.)

(VII.) $(MeO)_2C_{12}H_6SC{:}O \searrow SnCl_4 \nearrow O{:}CSH_6C_{12}(MeO)_2$

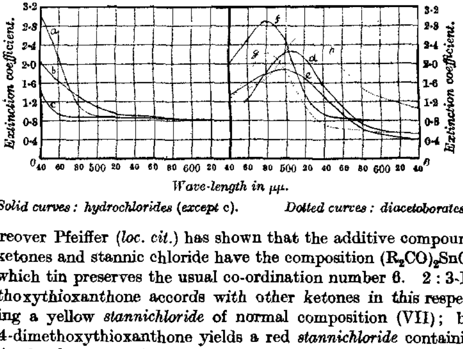


(VIII.)

Evidence in support of this view is forthcoming from independent sources. The absorption curves of the hydrochlorides of 1-methoxy-derivatives are characteristic and differ remarkably from those of the parent substances and from those of the hydrochlorides of other methoxythioxanthones. This is illustrated by the accompanying figures. Fig. 1 shows (*a* and *b*) the absorption curves of the hydrochlorides of 2 : 3-dimethoxy- and 2 : 3 : 4-trimethoxy-thioxanthones

with that of 1 : 4-dimethoxythioxanthone taken alone in alcohol (*c*); Fig. 2 illustrates the curves obtained from the hydrochlorides of 1 : 4-dimethoxy-(*d*), 4-hydroxy-1-methoxy-(*e*), and 1-methoxy-4-methyl-(*f*) thioxanthones. It is also remarkable that the diacetoborates of the 1-hydroxy-derivatives show absorption curves which are closely similar to those of the 1-methoxy-hydrochlorides; those obtained from the diacetoborates of 1 : 4-dihydroxy-(*g*) and 1-hydroxy-4-methoxy-(*h*) thioxanthones are shown also in Fig. 2. These diacetoborates undoubtedly possess (Dimroth, *Annalen*, 1926, **446**, 97) a co-ordinate ring (VI) of similar type to that now assigned to the 1-methoxy-hydrochlorides.

FIG. 1. FIG. 2.



Solid curves : hydrochlorides (except c). *Dotted curves : diacetoborates.*

Moreover Pfeiffer (*loc. cit.*) has shown that the additive compounds of ketones and stannic chloride have the composition $(R_2CO)_2SnCl_4$, in which tin preserves the usual co-ordination number 6. 2 : 3-Dimethoxythioxanthone accords with other ketones in this respect, giving a yellow *stannichloride* of normal composition (VII); but 1 : 4-dimethoxythioxanthone yields a red *stannichloride* containing equimolecular proportions of the reactants. Assuming that in this substance tin preserves the usual co-ordination number (6), it is evident that 1 : 4-dimethoxythioxanthone offers two centres of co-ordination (VIII); this is an essential feature of the structure proposed for the kation of the salts (V). In conclusion, it must be remarked that the structure as expressed is not meant to imply that the sulphur is without influence on the basic character of the thioxanthone nucleus; there is, on the contrary, evidence that this property is profoundly influenced by the state of the sulphur present. For example, the dioxides of the thioxanthones examined do not show basic character in the methods used in these experiments. A similar effect is evident in the character of 1-hydroxy-derivatives of thioxanthone. All those hitherto obtained are insoluble in aqueous alkali hydroxide, whilst the corresponding sulphones yield charac-

teristic red salts with this reagent. Another interesting feature of these 1-methoxy-derivatives of thioxanthone is found in the ease with which they are demethylated. This and other features will be the subject of a future communication.

Experimental.

1-Hydroxy-4-methoxythioxanthone (I).—*p*-Methoxyphenol (8 g.) was added in portions to a stirred solution of 2-thiolbenzoic acid (3 g.) in sulphuric acid (60 c.c.). After 15 minutes (15°), the mixture was poured into water (800 c.c.). The solid material was then digested with aqueous sodium hydroxide (2*N*), in which the required 1-*hydroxy-4-methoxy*-derivative was insoluble and 4-hydroxy-1-methoxythioxanthone and most impurities readily dissolved. The residue (*ca.* 50% of crude material) separated from acetic acid in orange-red needles, m. p. 182° (Found: C, 64·7; H, 3·9. $C_{14}H_{10}O_3S$ requires C, 65·1; H, 3·8%). The substance was insoluble in warm concentrated hydrochloric acid and did not yield a hydrochloride with the dry reagent. A perchlorate was not formed under the usual conditions. A purple sodium derivative was formed when sodium ethoxide was added to a benzene solution of the substance. The *acetyl* derivative, prepared in the usual way, had m. p. 138° (Found: C, 63·8; H, 4·0. $C_{16}H_{12}O_4S$ requires C, 64·0; H, 4·0%). The *diacetoborate* separated in deep red needles from a solution of the substance in acetic anhydride containing boroacetic anhydride; it had m. p. 205° and was decomposed by boiling water, yielding the original material (m. p. 182°). Analysis was made by weighing this product [Found: $C_{14}H_{10}O_3S$, 67·0. $C_{14}H_9O_3S{\cdot}B(O{\cdot}CO{\cdot}CH_3)_2$ requires $C_{14}H_{10}O_3S$, 66·8%].

1-Hydroxy-4-methoxythioxanthone dioxide,

$$C_6H_4{<}{}^{SO_2}_{CO}{>}C_6H_2(OH){\cdot}OMe,$$

was obtained when acetic acid containing the suspended thioxanthone and hydrogen peroxide (50% excess) was warmed (100°; 2 hrs.). It separated from the cooled liquid and after purification from acetic acid formed orange needles, m. p. 184° (Found: C, 57·7; H, 3·4. $C_{14}H_{10}O_5S$ requires C, 57·9; H, 3·4%). The sparingly soluble red sodium salt separated in needles from a hot solution in aqueous sodium hydroxide. The substance was also isolated from the alkylation of 1 : 4-dihydroxythioxanthone dioxide under intense conditions (J., 1928, 3158).

4-Hydroxy-1-methoxythioxanthone (II) was isolated from the crude material resulting from the condensation of *p*-methoxyphenol and 2-thiolbenzoic acid as described. This was treated with warm concentrated hydrochloric acid until the extract was no longer

coloured. The residue contained the isomeric 1-hydroxy-derivative, which was purified by alkali hydroxide as described in a previous paragraph. The cooled acid solution deposited the hydrochloride of the required substance; this was decomposed by hot water, and the resulting material, crystallised from alcohol, formed yellow needles, m. p. 270° (decomp.) (Found: C, 64·9; H, 3·8. $C_{14}H_{10}O_3S$ requires C, 65·1; H, 3·8%). The crimson *dihydrochloride* was obtained by reaction with dry hydrogen chloride (Found: HCl, 22·2. $C_{14}H_{10}O_3S,2HCl$ requires HCl, 22·0%) and the *perchlorate* was isolated by adding perchloric acid to a benzene solution of the substance which had been treated with hydrogen chloride (Found: $HClO_4$, 28·1. $C_{14}H_{10}O_3S,HClO_4$ requires $HClO_4$, 28·0%). Aqueous alkaline methylation readily yielded 1 : 4-dimethoxythioxanthone. A hot solution in acetic anhydride containing boroacetic anhydride deposited yellow needles of the *acetyl* derivative, m. p. 133° (Found: C, 64·0; H, 4·0. $C_{16}H_{14}O_4S$ requires C, 64·0; H, 4·0%); no boroacetate was obtained. Attempts to isolate the corresponding sulphone by oxidising the substance in acetic acid with hydrogen peroxide were unsuccessful, the material being decomposed. This result is in striking contrast to the behaviour of the 1-hydroxy-4-methoxy-derivative described above.

The stannichlorides were obtained by addition of stannic chloride to benzene solutions of the thioxanthone derivatives. The *stannichloride* of 2 : 3-dimethoxythioxanthone (VII) was isolated as yellow needles [Found: Sn, 14·8. $(C_{15}H_{12}O_3S)_2,SnCl_4$ requires Sn, 14·7%]. The *stannichloride* of 1 : 4-dimethoxythioxanthone (VIII) formed crimson needles (Found: Sn, 21·7. $C_{15}H_{12}O_3S,SnCl_4$ requires Sn, 22·3%), which were hydrolysed by water, yielding 1 : 4-dimethoxythioxanthone. Evidently demethylation similar to that effected by Pfeiffer in the case of the analogous stannichloride of alizarin dimethyl ether (*Annalen*, 1913, **398**, 141) had not taken place during the preparation of the substance.

The data referring to the relative stability of the salts of 1-hydroxy-4-methoxy- and 4-hydroxy-1-methoxy-thioxanthones were obtained under the conditions described in a former communication (this vol., p. 863) and are comparable with these.

The absorption spectra of the hydrochlorides (Fig. 1, *a* and *b*; Fig. 2, *d*, *e*, and *f*) were obtained from solutions of the respective thioxanthones in concentrated hydrochloric acid, and the spectra of the diacetoborates (Fig. 2, *g* and *h*) were obtained from solutions in acetic anhydride.

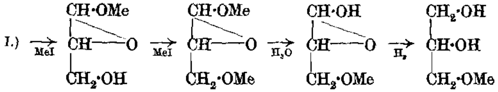
KING'S COLLEGE, LONDON. [*Received, May 15th, 1929.*]

CLXXIV.—*Methylation of* dl-*Glyceraldehyde.*

By H. GORDON REEVES.

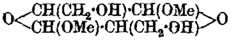
LTHOUGH *dl*-glyceraldehyde usually reacts in the bimolecular rm (Reeves, J., 1927, 2477), there are two possible structures for ie unimolecular form, *viz.*,

It seemed that complete methylation, hydrolysis, and reduction rould determine which of these represents the unimolecular form, or (I) should give α-methyl glycerol,



and (II) should give β-methyl glycerol, $OMe \cdot CH(CH_2 \cdot OH)_2$.

Unfortunately, it has as yet been found impossible to obtain a completely methylated derivative. A bimolecular *monomethyl* compound has been isolated for which the formula



is suggested, the secondary hydroxyl groups apparently being methylated with more ease than the primary ones.

Fischer and Taube (*Ber.*, 1927, **60**, 1704) obtained in good yield from the diacetyl derivative of glyceraldehyde a bimolecular methyl *cyclo*acetal, m. p. 158·5—159·5°, crystallising in needles, for which they suggested the formula $\left(O{<}\begin{matrix}CH \cdot CH_2 \cdot OH\\ CH \cdot OMe\end{matrix}\right)_2$. It does not agree in properties with the *compound* that has now been obtained by the methylation of glyceraldehyde at the ordinary temperature.

EXPERIMENTAL.

Methylation of Glyceraldehyde with Methyl Sulphate and Sodium Hydroxide.—In the apparatus described by Haworth (J., 1915, **107**, 11), a solution of 2 g. of glyceraldehyde in 90 c.c. of water was warmed to 35°, 1·6 c.c. of methyl sulphate were added, and 3·2 c.c. of methyl sulphate and 2·6 c.c. of 30% sodium hydroxide solution were simultaneously introduced during 3 hours. Thereafter the

following additions of methyl sulphate and the alkali solution were made: at 45°, 0·8 c.c. and 1·3 c.c.; after 12 hours, 0·8 c.c. and 1·3 c.c. at 55°; after 2 hours, 0 c.c. and 2·7 c.c., causing slight alkalinity; at 70°, 2·7 c.c. and 4·2 c.c. during 1 hour. The water-bath was finally boiled for ½ hour. After 48 hours, the reaction mixture had become brown and did not reduce Fehling's solution. A chloroform extract of it, after being dried with anhydrous magnesium sulphate and evaporated in a vacuum, gave a 10% yield of a pale yellow oil, which was soluble in water and did not reduce Fehling's solution [Found: OMe, 21·9; *M*, cryoscopic in water, 220. $(C_4H_8O_3)_2$ requires OMe, 29·8%; *M*, 209]. Refluxing with methyl iodide and silver oxide failed to augment the methoxyl content.

Formation of the Glucoside (Fischer, *Ber.*, 1893, **26**, 2400; 1895, **28**, 1145).—Glyceraldehyde (1·8 g.) was suspended in 5 g. of pure, acetone-free methyl alcohol and heated in a Carius tube at 100° for 24 hours. Next day, the yellowish-brown mixture was neutralised with silver carbonate and concentrated in a vacuum, a 50% yield of a non-reducing brown oil being obtained (Found: OMe, 22·3%; *M*, cryoscopic in water, 216). It was found impossible to methylate this oil further.

Methylation at Room Temperature (Haworth and Baker, J., 1925, **127**, 365).—A suspension of 5 g. of glyceraldehyde in 100 c.c. of pure methyl alcohol containing 4 g. of hydrogen chloride was shaken for 24 hours: the colourless solution obtained after 2 hours became yellow towards the end of the reaction. The excess of acid was neutralised (litmus) with silver carbonate, the filtrate evaporated to dryness in a vacuum, the crystalline product refluxed for 10 minutes in 50 c.c. of ethyl acetate, and the solution filtered. Next day, short colourless prismatic needles of a *monomethyl* derivative had been deposited (average yield in ten experiments, 5%), m. p. 204·5° after drying for a week over calcium chloride [* Found: C, 46·2; H, 7·7; OMe, 29·5; *M*, cryoscopic in water, 215. $(C_4H_8O_3)_2$ requires C, 46·2; H, 7·7; OMe, 29·8%; *M*, 209]. The monomethyl derivative is readily soluble in water and benzene, sparingly in chloroform and ligroin, and insoluble in ether. It does not reduce Fehling's or Benedict's solution even when hot, whereas the aldehyde is strongly reducing even in the cold. Attempts to methylate it further or acetylate it have been unsuccessful.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for a grant, to Professor W. N. Haworth, F.R.S., for the micro-analyses and for his help and

* These figures have been verified by micro-analyses.

advice, to Mr. J. Pryde, M.Sc., for his interest, and to Mr. E. T. Renbom, B.Sc., for his assistance in the latter part of the experimental work.

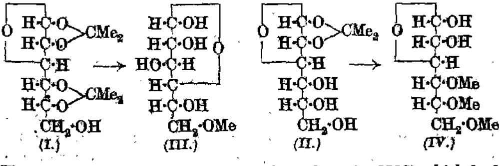
ST. BARTHOLOMEW'S HOSPITAL MEDICAL COLLEGE
(UNIVERSITY OF LONDON),
LONDON, E.C.1. [*Received, May 23rd*, 1929.]

CLXXV.—*The Constitution of Glucose-monoacetone, Glucose-diacetone, and of the Derived* 3 : 5 : 6-*Trimethyl Glucose and* 3-*Monomethyl Glucose.*

By CAMERON GORDON ANDERSON, WILLIAM CHARLTON, and WALTER NORMAN HAWORTH.

IN view of the preparation of sugar carbonates which exhibit many analogies with the sugar acetones (see forthcoming paper, Haworth and Porter), it has become imperative that the oxide-ring forms of sugars which participate in these types of condensation should be established.

Endeavours to provide an experimental proof of the structure of the glucose-acetones have hitherto been only partly successful. Recognising that glucose-monoacetone gave rise on methylation and hydrolysis to a product which was abnormal in its properties, Irvine and his collaborators (Irvine and Scott, J., 1913, **103**, 573; Irvine and Macdonald, J., 1915, **107**, 1710; Irvine and Patterson, J., 1922, **121**, 2146) considered the glucose-acetones to be derivatives of γ-glucose, and the following structures were advocated by the last-named authors for glucose-diacetone (I) and glucose-monoacetone (II).



(I.) (III.) (II.) (IV.)

These formulæ were intended to supplant those (p. 1333) which had been supported by Macdonald (J., 1913, **103**, 1896) and by Karrer and Hurwitz (*Helv. Chim. Acta*, 1921, **4**, 728) and strong criticism (herein shown to be groundless) was applied by Irvine and Patterson (*loc. cit.*) to the structures adopted by Karrer.

The monomethyl glucose derived from (I) was assigned the constitution (III), indicating the presence of the methyl group in position 6 in the chain; whilst the trimethyl glucose derived from (II) is, on this view, to be represented as 4 : 5 : 6-trimethyl glucose (IV). The experimental results purporting to establish the structure (III) for the monomethyl glucose have frequently been quoted as evidence for the presence of a free hydroxyl group at position 6 in glucose-diacetone (I), whether the latter be represented, as is here the case, as a propylene-oxide sugar derivative or as an ethylene-oxide form (Irvine and Patterson, *loc. cit.*).

The above experimental conclusions have been called into question by other investigators, who have adduced convincing evidence (*a*) that in glucose-diacetone a free hydroxyl group is not situated at the terminal position 6, (*b*) that the oxide-ring of the sugar cannot be attached at position 3, since the free hydroxyl group is allocated to this position, and (*c*) that the monomethyl glucose isolated from glucose-diacetone is 3-methyl glucose and not 6-methyl glucose (Freudenberg and Brauns, *Ber.*, 1922, **55**, 3233; Freudenberg and Doser, *Ber.*, 1923, **56**, 1243; Levene and Meyer, *J. Biol. Chem.*, 1922, **54**, 805; 1923, **57**, 317; 1924, **60**, 173).

The alternative formulæ advocated by these later authors ascribed to the glucose-acetones a 1 : 4-oxide ring, but a final proof of this assumption has been lacking. The recognition of γ-methylglucoside as a five-atom ring form rendered this hypothesis highly probable (Charlton, Haworth, and Peat, J., 1926, 89; Haworth, Hirst, and Miller, J., 1927, 2436), as did also the preparation, from the glucose-acetones as initial materials (Micheel and Hess, *Annalen*, 1926, **450**, 21), of a tetramethyl sugar having a similar rotation to that of tetramethyl γ-glucose.

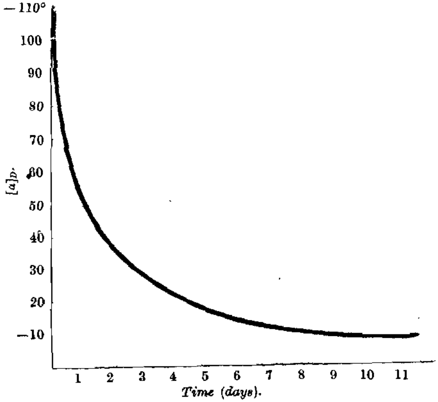
It seemed undesirable that the ring form of the sugar in the glucose-acetones should continue to be founded merely on analogy, and in the present communication it is experimentally demonstrated (1) that the above monomethyl glucose (a glucopyranose formed by ring-displacement from the furanose) is convertible into the usual crystalline tetramethyl glucopyranose; (2) that the trimethyl glucose derivable from glucose-monoacetone yields a crystalline *osazone*, and is 3 : 5 : 6-trimethyl glucose; (3) that this trimethyl glucose is a glucofuranose, since it is transformed readily into 2 : 3 : 5 : 6-tetramethyl γ-glucose (tetramethyl glucofuranose) and this again is converted into the crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone, which yields the crystalline phenylhydrazide of the corresponding acid. In the following discussion of results these new data are taken into account along with evidence adduced by Levene and by Freudenberg and their co-workers

(*locc. cit.*) for the recognition of the monomethyl glucose as 3-methyl glucose.

Curiously enough, on investigating the osazone of this monomethyl glucose we found its m. p. to be 178—179° and not 164—165° as given by Irvine and Scott (*loc. cit.*). This anomaly is disconcerting inasmuch as, on the evidence of its m. p. and other physical properties, this osazone is considered to be identical (*Irvine and Hynd, J.*, 1909, **95**, 1220) with that obtainable from the monomethyl fructose isolated by methylation and hydrolysis of

FIG. 1.

Mutarotation of the phenylosazone of 3-methyl glucose in ethyl alcohol ($c = 1{\cdot}1$).



α-fructose-diacetone. This contradiction has led us to examine the monomethyl fructose more closely, and the experimental results are described in the succeeding paper. Still further is this problem complicated by the observations of Helferich and Becker (*Annalen*, 1924, **440**, 1), who have also described Irvine and Scott's osazone as having m. p. 164—166° and have differentiated this from the osazone, m. p. 178—179°, of the supposed authentic 6-monomethyl glucose (compare also Kuhn and Ziese, *Ber.*, 1926, **59**, 2314).

It is now shown that the osazone from 3-monomethyl fructose also has m. p. 178—179° and not 164—165°, and that this has properties similar to those of the osazone of 3-monomethyl glucose.

It would thus appear, on the basis of the work of Helferich and Becker, that the 6-monomethyl glucose yielded fortuitously an osazone of the same m. p. A mixture of the osazones from 3-monomethyl glucose and 3-monomethyl fructose also melts at 178—179° without depression. Caution should be exercised, however, in accepting "mixed melting point" determinations of osazones as a means of confirming their identity, since the m. p.'s given are frequently merely decomposition temperatures.

We have, however, determined the mutarotation of the osazone from 3-monomethyl glucose and from 3-monomethyl fructose and from either source the osazone gives almost identically the same curve (see Fig. 1), showing the change − 109° ⟶ − 9°.

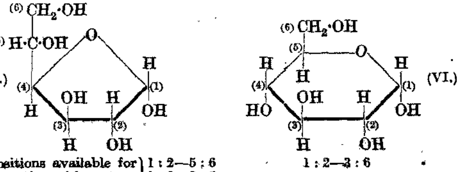
Discussion of Results.

It became apparent that the glucose-acetones should be accommodated by either of the structural forms of glucose: the pyranose and furanose types.

Moreover the isolation of 3 : 5 : 6-trimethyl glucose as described in the preceding section is at variance with the propylene-oxide formulæ (I) and (II) proposed by Irvine for the glucose-acetones.

Reference to the perspective formulæ of the two structural types of glucose (Drew and Haworth, J., 1926, 2305) furnishes some explanation of the occurrence of the glucofuranose form (V) in glucose-diacetone, inasmuch as the hydroxyl groups in glucopyranose (VI) are less favourably situated for the union with acetone.

(V.)



(VI.)

cis-Positions available for condensation with acetone groups: 1 : 2—5 : 6; 1 : 2—3 : 5; 1 : 2—3 : 6 (V.) — 1 : 2—3 : 6 (VI.)

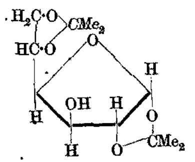
The formulation of glucose-diacetone as 1 : 2-3 : 6-diisopropylidene glucopyranose is inappropriate, since the monomethyl glucose derived from it should then be 4-methyl glucose, and this is rendered improbable by the work of Levene and his co-workers (*loc. cit.*). The glucofuranose having the acetone residues in positions 1 : 2-3 : 6 is also excluded as a possibility, since such a substance should

yield a 5-monomethyl glucose and this is found not to be the case inasmuch as further methylation of the monomethyl glucose gives rise to 2 : 3 : 4 : 6-tetramethyl glucopyranose.

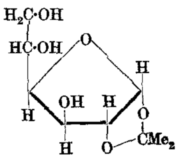
The latter result is consistent with the substitution of glucofuranose in the 1 : 2-5 : 6 or 1 : 2-3 : 5 positions (compare xylose-diacetone; Haworth and Porter, J., 1928, 611), in which case the monomethyl glucose would be substituted either at position 3 or 6. Now position 6 is excluded by the work of Freudenberg and of Levene (*loc. cit.*).

That the structural form of glucose in its acetone derivatives is that of glucofuranose is shown by the isolation of the 3 : 5 : 6-trimethyl glucose from glucose-monoacetone by methylation followed by hydrolysis. Earlier descriptions of this product lay stress on the ease with which it decomposes on distillation, and it is also credited with exceptional properties suggesting that it is not a trimethyl glucose but a trimethyl glucosone (Irvine and Macdonald, *loc. cit.*). None of these difficulties remains if the details for its preparation as given in the experimental section are adopted. The constitution of this trimethyl glucose is evident from its giving a crystalline *osazone* and also from its conversion into 2 : 3 : 5 : 6-tetramethyl glucofuranose. The latter is characterised by its transformation into the crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone, and into the crystalline phenylhydrazide of the 2 : 3 : 5 : 6-tetramethyl gluconic acid. It may be recalled that the constitutions of the lactone and acid were proved by oxidation methods (Haworth, Hirst, and Miller, J., 1927, 2436).

These results are sufficient to decide the position of the oxide-ring in glucose-monoacetone, and consequently also in the diacetone, and the following constitutional formulæ are therefore supported :



Glucose-diacetone.



Glucose-monoacetone.

It is seen that the glucose is here depicted as α-glucofuranose. The β-form of glucose could not undergo interaction to yield a second stereochemical form of glucose-diacetone, and it is conceivable that, if a second form of the diacetone should exist, it would be the structural isomeride, 1 : 2-3 : 5-*iso*propylidene glucofuranose. There

is at present no evidence for the existence of this possible second form.

EXPERIMENTAL.

Conversion of 3-Monomethyl Glucose into 2 : 3 : 4 : 6-Tetramethyl Glucose.—The glucose-diacetone used throughout the following preparations had the constants m. p. 109—110° and $[\alpha]_D^{17°}$ − 18·6°. Methylation either with Purdie's reagents or with sodium and methyl iodide (Freudenberg) yielded monomethyl glucose-diacetone, b. p. 105—106°/0·3 mm., $[\alpha]_D^{20°}$ − 31·4°, $n_D^{17°}$ 1·4518, OMe, 11·4 (Calc., 11·3%). Hydrolysis of this led to removal of the acetone groups, and the monomethyl glucose obtained (Irvine and Hogg, *loc. cit.*) had m. p. 160—161°, $[\alpha]_D^{17°}$ + 104·3° ⟶ 55·3° (after 19½ hours) (c = 1·33 in water) (Found: C, 43·3; H, 7·2; OMe, 15·9. Calc.: C, 43·3; H, 7·2; OMe, 16·0%).

1·2 G. of monomethyl α-glucose (m. p. 160—161°) were converted into the glucoside by heating in boiling methyl-alcoholic hydrogen chloride (1% HCl) for 4½ hours. The solution, which was then almost non-reducing, was neutralised with silver carbonate, filtered, and evaporated to a thick syrup, which contained colloidal silver. After the product had been dissolved in a little methyl alcohol, methyl iodide was added (not enough to cause precipitation of the glucoside) along with silver oxide and methylation was partly effected by heating at 45—50°. After another similar methylation the material was almost completely soluble in methyl iodide. Three further treatments with the Purdie reagents yielded a mobile oil.

This oil was hydrolysed by heating at 100° with 10 c.c. of 5% hydrochloric acid. The solution was neutralised with barium carbonate, evaporated to dryness, and the residue was extracted with chloroform. This solution yielded on evaporation a thick syrup which became solid. This was recrystallised and identified as tetramethyl glucose, m. p. 90—94° (yield, 0·6 g.), and gave the anilide, m. p. 135° (compare Irvine and Gilmour, J., 1908, 93, 1429).

The phenylosazone of 3-monomethyl glucose was prepared and recrystallised several times from aqueous alcohol (Found: C, 61·4; H, 6·7; N, 15·25; OMe, 8·5. Calc.: C, 61·3; H, 6·5; N, 15·05; OMe, 8·3%). Its m. p. was 178—179° and not 164—165° as quoted by Irvine and Scott (*loc. cit.*). Its change of rotation in ethyl alcohol was compared with that of the osazone derived from 3-monomethyl fructose and the values are expressed in the form of a graph in the introduction. It is conceivable that the osazones of a 6-monomethyl glucose and of a 3-monomethyl glucose might show great similarity both in the rate of mutarotation and in m. p. But the close agreement of the initial and the final rotation values

of each product appears in this case to suggest that the osazones are identical.

3 : 5 : 6-*Trimethyl Glucose and its Osazone*.—The use of β-glucose was found to be most advantageous for the rapid preparation of glucose-diacetone (Fischer and Rund, *Ber.*, 1916, **49**, 88). Glucose-monoacetone was prepared from the diacetone (Irvine and Scott, *loc. cit.*) and had the accepted physical constants (Fischer, *Ber.*, 1895, **28**, 2496).

In the preliminary methylation of glucose-monoacetone it is advisable to avoid the use of silver oxide and methyl iodide in acetone solution, because under these conditions there is a tendency for the glucose-diacetone to be regenerated. The methylated glucose isolated from this product by hydrolysis distils with decomposition and is far from homogeneous. It is possible that the difficulties of earlier authors (Irvine and Scott, Irvine and Macdonald, *locc. cit.*) are traceable to this cause. Consequently the methylation was conducted as follows: Glucose-monoacetone (30 g.) was dissolved in 150 c.c. of water and to this was admitted, with stirring, methyl sulphate (97 c.c.) and 33% sodium hydroxide solution (180 c.c.), the temperature being gradually raised from 20° to 60°. After the final heating at 60° for an hour, the cooled solution was extracted repeatedly with chloroform. The dried extracts were evaporated at 60° and yielded a pale yellow syrup, which was again submitted to similar methylation treatment. Thereafter the product had $[\alpha]_D$ − 29·5° (c = 1·55 in methyl alcohol); n_D 1·4470; OMe, 35·3%.

This specimen of trimethyl glucose-monoacetone (30 g.) was digested for 2 hours under reflux with 300 c.c. of aqueous methyl alcohol containing 0·5% of hydrogen chloride. The cooled solution was neutralised with silver carbonate, filtered, treated with charcoal and then with silica to remove traces of silver, and evaporated at 50°. The resulting trimethyl methylglucoside was collected (OMe, 50%) and hydrolysis was effected by digestion with 0·3% hydrochloric acid at 100° for 1½ hours, followed by neutralisation with barium carbonate and evaporation of the filtered solution at 60°. The trimethyl glucose was extracted with ether, and the product was distilled under 0·04 mm. without decomposition from a bath heated at 150—160° (b. p. about 134°). The distillate was a clear, almost colourless liquid (yield, 60%), showing $[\alpha]_D$ − 44·1° (c = 1·49 in ethyl alcohol) and − 25·9° (c = 1·3 in water); n_D = 1·4675 (Found: OMe, 41·1. Calc.: OMe, 41·9%).

Phenylosazone. 1 G. of the above 3 : 5 : 6-trimethyl glucose yielded 1·8 g. of crude *osazone*, which was dissolved in ethyl alcohol; the solution was treated with charcoal and diluted slightly with

water; matted yellow needles separated which, after recrystallisation from aqueous alcohol and drying in a vacuum at 45° until constant in weight, had m. p. 70—72° (Found: C, 62·8; H, 7·2; N, 14·15. $C_{21}H_{28}O_4N_4$ requires C, 62·95; H, 7·0; N, 14·0%).

Conversion of 3 : 5 : 6-Trimethyl Glucose into 2 : 3 : 5 : 6-Tetramethyl Glucose.—The trimethyl methylglucoside (10 g.) was methylated by solution in 50 c.c. of water and treatment at 60° with 20 c.c. of methyl sulphate and 17 c.c. of 50% sodium hydroxide solution. The extracted product (9·9 g.) was distilled, b. p. about 96°/0·025 mm., and yielded 8·2 g. of a colourless distillate having the constants $n_D^{16°}$ 1·4440, $[\alpha]_D^{16°}$ − 20·4° (c = 2·1 in water) (Found: OMe, 61·2. Calc. for tetramethyl methylglucoside: OMe, 62·0%).

Hydrolysis. The above product was hydrolysed by digestion at 95° with 0·3% hydrochloric acid for 1½ hours. The resulting sugar was isolated in the usual manner and on distillation under 0·08 mm. (bath temperature 150°) gave a colourless liquid having $n_D^{24°}$ 1·4500, $[\alpha]_D^{19°}$ − 14·3° (c = 1·26 in water) (Found: OMe, 51·5. Calc. for 2 : 3 : 5 : 6-tetramethyl glucose: OMe, 52·6%). About 60% of the product was distilled over, leaving a residue which crystallised, m. p. 97—98° (Found: OMe, 53·9%). This by-product has not yet been identified and is under investigation. It is probably a condensation product of the above tetramethyl glucose.

Oxidation. The above 2 : 3 : 5 : 6-tetramethyl methylglucoside (3 g.) was treated with an aqueous solution of bromine (1·5 c.c. in 20 c.c. of water) at 20° during 1½ days. It then no longer reduced Fehling's solution even after a preliminary heating with mineral acid. The solution was aerated to remove bromine, neutralised with silver carbonate, and filtered and the organic acid was liberated from its silver salt by titration with hydrochloric acid. The aqueous filtrate was then evaporated at 50°, the residue extracted with ether and evaporated, and the syrupy product thus isolated was heated at 70° for 5 hours and then distilled (2 g.). The colourless liquid crystallised on nucleation with 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone (compare Haworth and Long, J., 1927, 544) and had m. p. 25·5—26°, alone or in admixture with an authentic specimen prepared from octamethyl methyl-lactobionate.

Phenylhydrazide. The identification of the above 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone was assisted also by the preparation of this crystalline derivative. The lactone (0·4 g.) in ether was digested with 0·2 g. of phenylhydrazine. The resulting oil crystallised on cooling and from hot benzene gave colourless needles which, either alone or in admixture with an authentic specimen of the

phenylhydrazide of 2 : 3 : 5 : 6-tetramethyl gluconic acid (Haworth and Long, *loc. cit.*), melted at 136°.

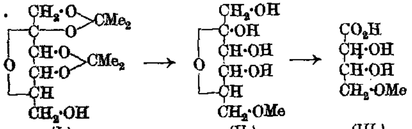
The authors are indebted to the Chemical Society for a grant for materials and to the Department of Scientific and Industrial Research for a maintenance grant to one of them.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, May* 18*th*, 1929.]

CLXXVI.—*The Constitution of α- and β-Fructose-diacetones. The Alleged Oxidative Degradation of the Derived Monomethyl and Tetramethyl Fructose.*

By CAMERON GORDON ANDERSON, WILLIAM CHARLTON, WALTER NORMAN HAWORTH, and VINCENT STANLEY NICHOLSON.

IRVINE and HYND (J., 1909, **95**, 1220) in their investigations on the structure of α-fructose-diacetone (Fischer, *Ber.*, 1895, **28**, 1164) prepared a monomethyl derivative of the compound, and by elimination of the two acetone residues isolated a crystalline monomethyl fructose, m. p. 122—123°, $[\alpha]_D^{20°}$ $-70{\cdot}5° \longrightarrow -53{\cdot}1°$. In repeating this preparation, we have isolated a sugar having the same constants, but after several recrystallisations the monomethyl fructose gave the following data: m. p. 128—130°, $[\alpha]_D^{20°}$ in water $-84{\cdot}1° \longrightarrow -53{\cdot}5°$. The phenylosazone had m. p. 177—179° (Irvine and Hynd, *loc. cit.*, give m. p. 142—144°; and Irvine and Scott, J., 1913, **103**, 573, m. p. 164—165°). Irvine and Hynd recorded that, when oxidised with bromine water, monomethyl fructose gave as the principal product an acid recognised as αβ-dihydroxy-γ-methoxybutyric acid (III). This was fully analysed, titrated, and examined also as the barium salt. From these data they concluded that the constitution (II) should be assigned to monomethyl fructose, and therefore that the formula (I) should be allocated to α-fructose-diacetone.



(I.) (II.) (III.)

This work has been supplemented by further experiments (Irvine

and Patterson, J., 1922, **121**, 2146) which go to show that both α-fructose-diacetone and the monomethyl fructose derived from it are derivatives of normal or ordinary fructose.

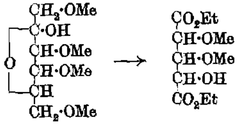
It is evident that if these experimental data could be substantiated, *and if the formula (II) assigned to the monomethyl fructose were to* hold, this would preclude the formulation of this normal fructose derivative as a 2 : 6-oxide or pyranose form, inasmuch as position 6 is occupied by a methyl group and therefore is not available for the attachment of the oxide ring. This problem has assumed importance in view of the determination of the ring structure of normal fructose by Haworth and Hirst (J., 1926, 1858) and by Haworth, Hirst, and Learner (J., 1927, 1040), who have demonstrated that normal fructose derivatives can only be formulated as a pyranose or 2 : 6-ring structure.

We have therefore deemed it advisable to repeat the work of Irvine and Hynd and, observing their conditions, we attempted to oxidise monomethyl fructose by agitating a solution of the sugar *in the cold with* bromine water, but we were surprised to find that the monomethyl fructose was recovered unchanged. Proceeding on the assumption that a more prolonged contact with the reagent was necessary to imitate the result described by Irvine and Hynd, we again repeated the experiment, at a higher temperature, keeping the monomethyl fructose in contact with bromine water with frequent agitation during 12 days. At the end of this period *a negligible amount of an acid product was formed*, and the monomethyl fructose was recovered unchanged in almost quantitative yield.

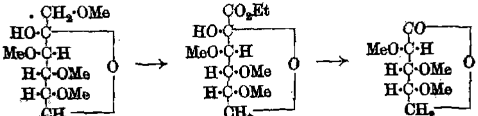
Endeavouring to explain the account given by Irvine and Hynd of the properties of their acid product, we subjected the regenerated monomethyl fructose to the same analytical tests as did the earlier authors. It is known that fructose reacts with bases to give *complex substances*, and we *observed similarly* that monomethyl fructose combined with barium hydroxide, and this explains the observation of Irvine and Hynd, who considered they had prepared a barium salt of their supposed degradation product. They appear to have been misled in supposing that the sugar underwent any appreciable degradative oxidation by the agency of cooled bromine water. The "principal product" recovered from the contact with *bromine* must have consisted almost entirely of unchanged monomethyl fructose. The stability of the monomethyl fructose is indeed only to be expected in view of the fact, which has long been known, that fructose itself exhibits a remarkable stability in contact with bromine water under the conditions described by Irvine and Hynd (Kiliani, *Annalen*, 1880, **205**, 145,

180; Bertrand, *Compt. rend.*, 1909, **149**, 225). Similarly the normal tetramethyl fructose and even its labile or γ-form are almost inert towards this reagent under these conditions.

In support of their view that α-fructose-diacetone should be represented by the structural formula (I) Irvine and Patterson (*loc. cit.*) described *the transformation of this substance into the* monoacetone and, by methylation of the latter, into trimethyl fructose-monoacetone. The removal of the remaining acetone residue, followed by further methylation and hydrolysis, led to the isolation of the crystalline normal tetramethyl fructose, identical with that which had previously been isolated by the methylation of methylfructoside by Purdie and Paul (J., 1907, **91**, 289). In a subsequent paper Irvine and Patterson (J., 1922, **121**, 2696) submitted this crystalline tetramethyl fructose to oxidation with nitric acid and isolated a compound, m. p. 86—87°, which they designated diethyl dimethoxyhydroxyglutarate (V). On the basis of this work they ascribed to the methylated sugar the constitution represented by 1 : 3 : 4 : 6-tetramethyl fructose (IV).

(IV.)  (V.)

On repeating this work Haworth, Hirst, and Learner (J., 1927, 1040) isolated the same crystalline derivative having m. p. 87—88° and adduced evidence that this was not the diethyl ester of the substituted glutaric acid (V) but the monoethyl ester of a lactol acid formulated as the trimethyl fructuronic acid (VII). A confirmation of this view is now communicated in that it is shown that the crystalline oxidation product (VII) can be degraded by contact with acid permanganate to the crystalline d-2 : 3 : 4-*trimethyl* δ-*arabonolactone* (VIII).



(VI.) (VII.) (VIII.)

The identification of this product (VIII) was assisted by the circumstance that we had already obtained the corresponding

l-enantiomorph (Drew, Goodyear, and Haworth, J., 1927, 1244), and the properties of these two substances are compared below :

	d-2 : 3 : 4-Trimethyl δ-arabonolactone (from crystalline 1 : 3 : 4 : 5-tetramethyl fructose).	*l*-2 : 3 : 4-Trimethyl δ-arabonolactone (from *l*-arabinose).
Crystalline form	Long, colourless needles	Long, colourless needles
M. p.	44°	45°
$n_D^{18°}$ (superfused)	1·4626	$n_D^{15·5°}$ 1·4630
$[\alpha]_D^{18°}$ (initial)	−177·3°	$[\alpha]_D^{21°}$ +179·5°

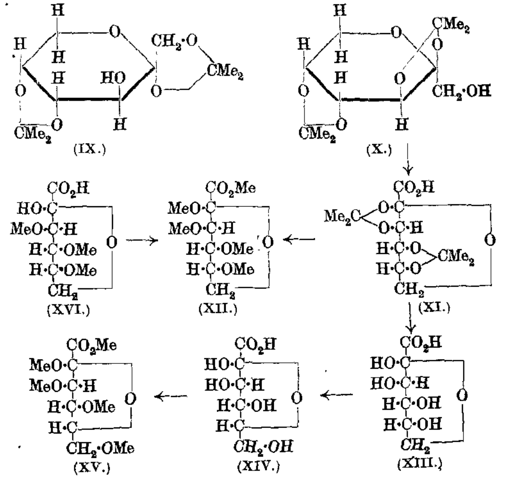
This comparison leaves little doubt that our product was the stereoisomeride of the *l*-2 : 3 : 4-trimethyl δ-arabonolactone which had previously been prepared and we have also confirmed the identity of our *d*-2 : 3 : 4-trimethyl δ-arabonolactone by the preparation of it from *d*-arabinose (forthcoming paper by Haworth and Jones). Moreover the *d*-lactone has also been submitted to oxidation and has been shown to give rise to *d*-*arabo*-trimethoxyglutaric acid, characterised through its crystalline methylamide.

It is therefore clear that no conclusion can be reached other than that the tetramethyl fructose is to be represented as 1 : 3 : 4 : 5-tetramethyl fructopyranose (VI). This view is in agreement with the constitution (IX) now supported for α-fructose-diacetone.

The view that the monomethyl fructose derived from α-fructose-diacetone should be formulated as 3-methyl fructose and that in α-fructose-diacetone the substituted residues occupy the hydroxyl positions 1 : 2 and 4 : 5 (Freudenberg and Hixon, *Ber.*, 1923, **56**, 2119; Freudenberg and Doser, *ibid.*, p. 1243) is confirmed by these results (see preceding paper).

That the action of nitric acid on crystalline tetramethyl fructose (VI) should be principally to effect the oxidation of the $-CH_2·OMe$ group in position 1 to carboxyl, was previously commented upon as a striking observation, especially so since the hydroxyl group in position 2, commonly designated the " reducing group " in fructose, evaded attack in this instance. It may be reflected, however, that the state of oxidation of the reducing group differs from that of an ordinary aldose sugar and may, indeed, in a sense be regarded as already completely oxidised in its condition as a potential keto-group. The tendency of fructose derivatives to undergo initial oxidation at the position 1 is also indicated in the series of experiments we have conducted on β-fructose-diacetone. The latter has been shown by Ohle (*Ber.*, 1925, **58**, 2577) to undergo oxidation with permanganate to the corresponding diacetone-fructuronic acid (XI), which on elimination of its acetone groups gave the unsub

stituted fructuronic acid (XIII). We have examined the product (XI) and have shown that by simultaneous hydrolysis and methylation it gives rise to the crystalline methylated methyl ester (XII) which had previously been prepared by one of us from the lactol acid (XVI) (Haworth, Hirst, and Learner, *loc. cit.*). This experiment connects Ohle's results with our previous observations on the oxidation of crystalline tetramethyl fructose and



demonstrates that the oxidation of this sugar proceeds initially in the same way as the oxidation of β-fructose-diacetone. We regard the isolation by Ohle and his co-workers of the unsubstituted fructuronic acid (α-keto-gluconic acid) as being of special interest in this connexion, and the high lævorotation of this product seems to require that it should be represented preferably by the cyclic formula (XIII) rather than by the open-chain formula. There is, indeed, no doubt that on careful methylation it passes to the cyclic lactol ester (XII) which we have characterised through its identity with the crystalline substance obtained on esterifying and methylating the lactol acid (XVI).

Under other conditions, involving treatment of the fructuronic

acid with mineral acid, followed by methylation, we isolated a liquid ester which seemed to be an isomeride and had a lower boiling point. This we have identified as the five-membered ring isomeride formulated as in (XV), which was previously obtained by *one of us by the oxidation of tetramethyl γ-fructose.* That this was so was demonstrated by conversion into its crystalline amide, m. p. 100—101°, which was shown to be identical with the crystalline amide isolated in the course of earlier work on the oxidation of tetramethyl γ-fructose (Haworth, Hirst, and Nicholson, J., 1927, *1513*; compare also p. 2308).

It is further demonstrated that Ohle's fructuronic acid can be represented by the six-membered ring formula (XIII), and that this in contact with dilute sulphuric acid can modify its ring structure to give a five-membered ring acid (XIV). This displacement of the original ring structure corresponds exactly to the change which accompanies the formation of γ-methylfructoside from ordinary fructose.

EXPERIMENTAL.

α-Fructose-diacetone and the Derived Monomethyl Fructose.—α-Fructose-diacetone, prepared by Fischer's method (*loc. cit.*), was methylated with methyl iodide and silver oxide, giving monomethyl α-fructose-diacetone having the constants given by Irvine and Hynd (*loc. cit.*), and the removal of the acetone residues was effected as described by these authors. The product was a crystalline monomethyl fructose, m. p. 122—123°, but after several recrystallisations the m. p. was raised to 128—130°, with slight sintering at 122°. $[\alpha]_D^{20^\circ}$ in water ($c = 0{\cdot}92$) $-84{\cdot}1°$ (after 15 mins.) ⟶ $-53{\cdot}5°$ (Found: C, 43·2; H, 7·3; OMe, 16·0. Calc.: C, 43·25; H, 7·2; OMe, 16·0%). This sugar gave a phenylosazone, m. p. 165—169° before purification; but when it was recrystallised from aqueous ethyl alcohol its m. p. was raised to 177—179° (Irvine and Hynd give m. p. 142—144°, and Irvine and Scott, J., 1913, **103**, 573, give m. p. 164—165°. Compare also the preceding paper by Anderson, Charlton, and Haworth) (Found: C, 61·3; H, 6·7; OMe, 8·3; N, 15·1. Calc.: C, 61·3; H, 6·45; OMe, 8·3; N, 15·05%).

1 G. of the crystalline monomethyl fructose was dissolved in a little water and the solution was cooled and stirred during the addition of 2 g. of bromine dissolved in 60 c.c. of water. The operation occupied 8 hours. The solution having been kept exposed to the atmosphere over-night, loss of bromine was made good by the addition of a further quantity, and the solution was again shaken for 24 hours. The solution, still strongly reducing, was then evaporated at 40—50° under diminished pressure to half bulk, diluted, and again reduced to half bulk, this procedure being

repeated four times. Thereafter the solution was neutralised with silver carbonate, filtered, treated twice with hydrogen sulphide and then with charcoal, and filtered. The colourless neutral solution was evaporated under diminished pressure to a thick syrup, which reduced Fehling's solution strongly. On keeping, this syrup crystallised, and recrystallisation of the crude material from ethyl acetate gave monomethyl fructose (yield, 85%), m. p. 126—128° both alone and when mixed with the original material.

Since the conditions of the experiment had not been effective in promoting oxidation, they were modified in order to give prolonged contact with bromine water at an elevated temperature. Accordingly, the operation was repeated, 4 g. of monomethyl fructose being dissolved in water and 9·5 g. of bromine in water added with stirring during 1 hour. The solution was shaken during 24 hours without cooling, and was then kept for 40 hours at 18—20°. A test sample having shown that the product still reduced Fehling's solution strongly, the solution was kept at 25—30° for 1 day. More bromine water was added, but after 12 days, during which the reagents had been in contact, the reducing property had not disappeared. The hydrogen bromide was removed by means of litharge, and the solution was filtered, shaken with silver oxide, again filtered, and treated with charcoal. The filtrate was now treated with hydrogen sulphide. A negligible quantity of silver sulphide was precipitated, indicating that very little organic acid was present as silver salt and that oxidation of the sugar had not taken place to an appreciable extent. The colourless solution was evaporated at 50°, and the residual syrup dissolved in water and digested at 70° with precipitated calcium carbonate, which neutralised the very faint acidity. The filtrate was evaporated to 5 c.c. and diluted with 100 c.c. of alcohol, which precipitated a slight film of a calcium salt (less than 0·1 g.). No calcium salt remained in the filtrate, and the latter was evaporated and yielded a syrup which became crystalline. Recrystallisation from ethyl acetate gave unchanged monomethyl fructose, m. p. 126—128°, identical with the original material and almost undiminished in quantity.

To confirm its identity, the regenerated sugar was converted into the diacetone compound by treatment with acetone containing 0·4% of hydrogen chloride. The product was isolated in the usual way and yielded crystals, m. p. 114—115°, $[\alpha]_D^{\circ}$ — 134·5° (*Found*: C, 57·1; H, 8·1; OMe, 11·7. Calc.: C, 56·9; H, 8·0; OMe, 11·3%).

Irvine and Hynd assumed the presence of about 6% of tartaric anhydride in their oxidation product, which assumption enabled them to bring their analytical figures into closer agreement with the theoretical figures.

A solution containing monomethyl fructose (0·2485 g.) and 20 c.c. of 0·42*N*-barium hydroxide was heated on a water-bath for 5 minutes; it was then cooled and, although dark in colour, was neutralised with *N*-hydrochloric acid by titration in presence of phenolphthalein. This showed that 0·104 g. of barium had been retained by the sugar.

Again, monomethyl fructose (0·4798 g.), dissolved in water, was heated during 5 minutes at 100° in the presence of 15 c.c. of 0·42*N*-barium hydroxide. The solution was cooled, carbon dioxide admitted to remove excess of barium hydroxide, and the solution filtered. Titration of this solution indicated the presence of 0·266 g. Ba. It would thus appear that the monomethyl fructose had combined with barium hydroxide, and Irvine and Hynd's titration results and barium estimations are explicable without the need of assuming that any oxidation with bromine to an organic acid had taken place.

Oxidation of Tetramethyl Fructopyranose.—Crystalline tetramethyl fructose, m. p. 98—99°, $[\alpha]_D$ − 124° (in water), was oxidised with nitric acid (*d* 1·2) at 90° under the conditions described by Haworth, Hirst, and Learner (*loc. cit.*), and the lactol acid, $C_9H_{16}O_7$ (XVI), was converted into the crystalline ethyl ester, $C_{11}H_{20}O_7$, m. p. 87—88°, $[\alpha]_D$ − 98° in water. This product was identical with that described by Irvine and Patterson (*loc. cit.*) as the ethyl ester of a dibasic acid, but which has since been shown to be the ethyl ester of the monobasic acid above mentioned (Haworth and Hirst, J., 1926, 1858). The crystalline ester (1·6 g.) was hydrolysed by heating with 2/3*N*-sulphuric acid (12 c.c.) at 85° for 2½ hours. A further quantity of 12 c.c. of 2/3*N*-sulphuric acid was then added along with 11·2 c.c. of a solution of barium permanganate (900 c.c. of solution were equivalent to 8 g. of oxygen), which was slowly admitted from a burette, and the solution was constantly shaken. This quantity of permanganate was calculated to provide one atomic proportion of oxygen for the oxidation of the liberated organic acid. The solution was then made alkaline with baryta and kept for some hours, and the excess of baryta was removed by admitting carbon dioxide. The precipitated barium salts were collected and washed, and the filtrate and washings were concentrated under diminished pressure. The concentrated solution, containing the barium salt of an organic acid, was treated with sufficient dilute sulphuric acid to precipitate the whole of the barium as sulphate. The filtrate was evaporated under diminished pressure, and the organic residue was dissolved in warm dry ether. This solution was filtered, the ether evaporated, and the viscid residue distilled under 0·05 mm. The colourless distillate solidified

on keeping, and after draining on porous tile in a cool dry atmosphere, the product was obtained as long needles, m. p. 44°. It showed $[\alpha]_D^{18°}$ − 177·3°, diminishing to − 111·4° (after 1 hour), − 83° (2 hours), − 10·2° (2 days). The general appearance, crystalline form, and melting point were identical with those displayed by the enantiomorphous *l*-2 : 3 : 4-trimethyl δ-arabonolactone, and the latter also showed $[\alpha]_D^{21°}$ 179·5° in water (c = 1·41). The rate of hydration or mutarotation also corresponded with the recognition of this substance as d-2 : 3 : *4-trimethyl δ-arabonolactone* (Found : C, 50·25; H, 7·5; OMe, 46·9. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%).

Experiments with β-*Fructose-diacetone.*

(A) *Combined Hydrolysis and Methylation of Potassium Fructuronate-diacetone. Isolation of Methyl Tetramethyl Fructuronate* (XII) *and the Crystalline Amide.*—The above potassium salt was prepared from 10 g. of β-fructose-diacetone (m. p. 97°. Found : C, 55·4; H, 8·1%) by oxidation with alkaline permanganate (yield, 8 g.) (Ohle, *loc. cit.*).

The potassium salt (6 g.), dissolved in 20 c.c. of water, was heated at 40° during stirring in presence of 5 c.c. of methyl sulphate. After 15 minutes, 10 c.c. of 30% sodium hydroxide solution were added and the temperature was raised to 60°. Methylation was then continued in the usual way at 70°, 25 c.c. of methyl sulphate and 50 c.c. of 30% sodium hydroxide solution being used. The solution was finally heated at 100° for ½ hour, cooled, and acidified with dilute sulphuric acid until it gave a faintly acid test with Congo-red. An equal volume of ethyl alcohol (rectified spirit) was added and the sodium sulphate was thus precipitated. The filtrate was concentrated to 20 c.c. and the methylation process repeated in the above manner, but without the preliminary heating in presence of methyl sulphate.

The product was thereafter extracted in the usual way and submitted to further treatment with Purdie's reagents. The resulting liquid substance was collected and distilled (b. p. 100—103°/ 0·05 mm., $n_D^{20°}$ 1·4532); it then crystallised on nucleation with a specimen of methyl tetramethyl fructuronate (XII) (Haworth and Hirst, J., 1926, 1858). Recrystallisation of this specimen from ether gave colourless hexagonal plates, $[\alpha]_D^{22°}$ − 130° (in water); m. p. 102—103° either alone or in admixture with a specimen obtained by oxidation methods from normal tetramethyl fructose by Haworth and Hirst (Found : C, 50·3; H, 7·7; OMe, 55·7. Calc. : C, 50·0; H, 7·6; OMe, 58·7%).

Formation of Tetramethyl Fructuronamide.—A methyl-alcoholic

solution of the above methyl ester was saturated with dry ammonia at 0° and kept for 5 days. Evaporation of the solvent yielded the crystalline amide, m. p. 118—119°, which has already been described by Haworth, Hirst, and Learner (*loc. cit.*) and formulated as a six-atom ring form obtainable from tetramethyl fructopyranose.

(B) *Methylation of Fructuronic Acid.*—The potassium salt (8 g.) already mentioned above was dissolved in 120 c.c. of *N*-sulphuric acid and heated at 45° for 24 hours. The two acetone residues were thus eliminated from the liberated fructuronic acid-diacetone, the hydrolysis being followed by means of polarimetric observations. The cooled solution was neutralised, and submitted to methylation with methyl sulphate and alkali, and finally with methyl iodide and silver oxide. The extracted syrupy product gave the following fractions on distillation under 0·17—0·13 mm.: (1) 1·2 g., b. p. 87°, $n_D^{14°}$ 1·4490; (2) 2·7 g., b. p. 96—98°, $n_D^{14°}$ 1·4550; (3) 0·45 g., b. p. 100°, $n_D^{14°}$ 1·4617. The fractions (2) and (3) crystallised spontaneously and after draining on porous tile and purification from ether gave colourless plates, m. p. 101—102°, identical with the methyl tetramethyl fructuronate (XII), m. p. 102—103°, described above under (A). Fraction (1) was dissolved in dry methyl alcohol and saturated at 0° with ammonia. After the solution had been kept for 3 days, the solvent was evaporated; the residual syrup on extraction with light petroleum, yielded the highly characteristic long needles of the amide, having m. p. 100—101° alone or when mixed with the specimen prepared by Haworth, Hirst, and Nicholson (*loc. cit.*) from tetramethyl γ-fructose. More of this amide was prepared from the material absorbed by porous tile from the crystallised fractions (2) and (3). It was evident, therefore, that prolonged contact of the potassium salt with dilute sulphuric acid had led to displacement of the oxide-ring in a portion of the products inasmuch as the amide, m. p. 100—101°, has been shown by Haworth, Hirst, and Nicholson to be a derivative of a five-atom ring form obtainable from tetramethyl fructofuranose.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, May 18th, 1929.*]

First Pedler Lecture.

DELIVERED ON MAY 30TH, 1929.

By WILLIAM HENRY PERKIN, Sc.D., LL.D., F.R.S.

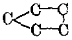
The Early History of the Synthesis of Closed Carbon Chains.

WHEN I was asked to deliver the first Pedler Lecture I was disinclined to accept the honour because it was clear to me that I could only speak with any authority on some branch of Organic Chemistry with which I had been closely associated and I saw at once that it would be very difficult to select from this field a subject which could be dealt with adequately and in an interesting manner in the course of a single lecture. During recent years, my own researches have been mainly concerned with the determination of the structure and the subsequent synthesis of alkaloids belonging to the berberine, cryptopine group and although, after I had accepted the invitation, I made more than one attempt to see whether it might be possible to sketch in a quite general way the methods which are now available for the synthesis of such alkaloids, I was in the end obliged to give up the idea, mainly because I found that it was quite impracticable to hope to deal with the matter at all effectively during the time at my disposal.

I then thought of a suggestion which had often been made to me by Professor Robinson and other friends that I should take advantage of a suitable occasion to give some account of my recollection of the early history of the experiments on the Synthesis of Closed Chains and of the difficulties which were met with in the development of the work, since it appears that nothing dealing with this aspect of the subject has ever been published. I have always felt that the obvious and indeed very serious objection to my giving a lecture of this kind is that it means talking a good deal about myself and necessitates a rather detailed account of the origin and development of much of my own experimental work. However, on looking through some of the lectures which have been delivered before the Society and are printed in the Journal, I was rather relieved to find that others who had evidently experienced the same difficulty had not hesitated to discuss, in some cases in considerable detail, their own views and experiments when the subject matter of the lecture seemed to necessitate such a course. With this encouragement and after talking the matter over with several of my colleagues, I decided to waive the objections I have to the introduction of so much matter of a personal kind and I propose, with your permission, to give you a brief account of what happened

in those early days and of the train of thought which led to the inception and gradual development of the researches on the synthesis of closed carbon chains. It will be necessary that I should confine myself strictly to the early history of the subject and I must not attempt to say anything about the vast developments which have taken place since those early days and especially during recent years.

For many of us, most of all perhaps for the younger generation of chemists, it must be very difficult to appreciate the fact that, not so many years ago—certainly not more than 50 years ago—the idea was firmly fixed in the minds of chemists that Organic Chemistry must be sharply divided into two sections, namely, the Fatty Series, comprising open chains like hexane, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, and their derivatives, and the Aromatic Series, consisting of the 6-carbon ring benzene and its derivatives. It was thought to be so out of the question that intermediate carbon rings containing 3, 4, or 5 atoms

or 

could be capable of existence that no one seems to have given them serious attention or to have attempted to construct them. Thus we find Victor Meyer in 1876 writing an interesting paper in the *Annalen* (**180**, 192) in the course of which he emphasises the fact that interactions which might conceivably have led to the formation of the 3-carbon ring had invariably resulted in the production of the isomeric unsaturated open-chain substances. It is quite clear from this paper that Victor Meyer was, in those days, firmly persuaded that the 3-carbon ring is incapable of formation and that he also held the opinion that there was no evidence to warrant the supposition that other rings smaller than six are ever likely to be obtained.

Shortly after going to Germany in 1880, I happened to translate this paper, largely for the sake of practice in German, and was much impressed by the interesting way the subject was presented and by the arguments and views brought forward by Victor Meyer. After studying for two years in Würzburg under Wislicenus, I went to Munich to continue research under Baeyer and was set the task of attempting to make benzoylacetic ester. This substance was ultimately prepared, as you all know, by making use of a method which arose out of his indigo work and was suggested to me by Baeyer, namely, by treating phenylpropiolic ester with sulphuric acid and pouring the mixture on ice, and I shall presently show that this research had some bearing on the subsequent work on ring

formation. Soon after I had started work in Munich, I think it was in November 1882, Victor Meyer paid one of his frequent visits to Baeyer's laboratory and I then ventured to remind him of his paper in the *Annalen* and to ask him whether he was still of the same opinion or whether he had altered or modified his views. He was kind enough to ask me to supper and to spend the rest of the evening at the Hofbräuhaus with him and I remember the occasion as if it had occurred only yesterday. It was of course a great opportunity and privilege for so young a student as I then was to be invited to spend the evening and talk chemistry with a man of such eminence. During and after the simple meal he discussed the matter of ring formation in great detail and with his usual nervous energy, emphasising in particular the absence of any evidence of the existence of rings made up of 3, 4, or 5 carbon atoms, and when I told him that it was my intention to attempt to prepare substances containing such rings, he said he was much impressed by my enthusiasm but thought I should be well advised at so early a stage in my career to work at something more promising and more likely to give positive results.

Victor Meyer's main argument, to which he returned over and over again, was this, that if rings smaller than 6 are capable of formation and are stable enough to exist, how was it that nothing was known about them? He pointed to the large amount of synthetical work which had already been done in so many directions and emphasised the fact that while such synthetical work had not infrequently led to the formation of derivatives of benzene, as, for example, in the case of the conversion of acetone into mesitylene, no such condensations had so far been met with which had resulted in the formation of rings containing less than 6 carbon atoms. Next morning, I told Baeyer about the conversation I had had the previous evening with Victor Meyer and it was quite clear that he also held the same views and was in general agreement with the arguments which Victor Meyer had brought forward. He saw no reason why we should assume that rings containing a smaller or larger number of carbon atoms than six are capable of existence; on the contrary, all experience was against such an assumption. If substances derived from such rings are possible and have reasonable stability, how was it, I particularly remember his saying, that they had never been met with in Nature?

However, I am quite sure that Baeyer, even at that time, was not completely satisfied with the position he had taken up, because soon afterwards and on more than one occasion he asked me if I was still interested in the possible existence of the smaller rings and made some encouraging remarks when I told him I was hoping to start

work on them in a short time. Moreover he evidently discussed the matter with Emil Fischer, because on one of the occasions when Emil Fischer visited the Munich laboratories and had been talking to me about the work on benzoylacetic ester and especially about the isolation of dibenzoylmethane, in which he was particularly interested, he told me as he was leaving that Baeyer had spoken to him about my wish to start synthetical work on the formation of derivatives of the smaller carbon rings. He thought it unlikely that I should succeed in obtaining such substances and said that even if they were formed in small quantity they would probably exhibit little stability and it would be very difficult to demonstrate their existence sufficiently conclusively to convince the chemical world.

The investigation of benzoylacetic ester, on which I was engaged at that time, proved to be tedious and often very disappointing, partly on account of the difficulty associated with the preparation of the crude ester in any quantity, but mainly because the method of fractional distillation under low pressure had not then been developed and consequently it was almost impossible to obtain any of the oily substitution derivatives in a state even of approximate purity.

The plan I adopted was to carry out each new experiment in the first place with acetoacetic ester and then to apply the experience I had obtained to the case of benzoylacetic ester. In the course of the preparation of dipropylacetoacetic ester, I had made a quantity of the monopropyl derivative, $CH_3\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)\cdot CO\cdot CH_3$, from propyl bromide by the usual process : and was proposing to introduce the second propyl group in a similar manner when it occurred to me that, if this mono-substitution derivative could be brominated at the end of the chain, the sodium derivative of the product might decompose with elimination of sodium bromide and formation of acetyltetramethylenecarboxylic ester containing the 4-carbon ring :

$$CH_2Br\cdot CH_2\cdot\begin{matrix}CH_2\\Na\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CO\cdot CH_3\\CO_2Et\end{matrix} \longrightarrow CH_2\!<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CO\cdot CH_3\\CO_2Et.\end{matrix}$$

As there was clearly no prospect of discovering a process for introducing the bromine atom into the end position in the propyl group of propylacetoacetic ester, the only alternative seemed to be to start with a dibromide containing the two bromine atoms in the required positions, that is to say, to start with trimethylene bromide, $CH_2Br\cdot CH_2\cdot CH_2Br$. Then the ring formation might take place in the way I have just indicated.

It happened that at that time I had in my possession small

quantities of ethylene bromide, propylene bromide and trimethylene bromide as well as of other bromides and iodides which had been prepared with quite a different object in view, namely, that of determining the relative stability of the halogen atoms on heating with water, dilute alkalis, etc. I had already made preliminary experiments on these lines which seemed to promise interesting results, but the research was never developed. With my small supply of trimethylene bromide, I carried out the condensation with the sodium derivative of acetoacetic ester and obtained to my surprise and delight a small quantity of an ester which, on analysis, gave numbers agreeing with those required for acetyltetramethylene-carboxylic ester.

Since this substance is a disubstituted acetoacetic ester, I expected that hydrolysis with alkali would lead to the formation of acetyl-tetramethylene and tetramethylenecarboxylic acid,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}CH{\cdot}CO{\cdot}CH_3 \text{ and } CH_2{<}{}^{CH_2}_{CH_2}{>}CH{\cdot}CO_2H,$$

but the sole product of hydrolysis was a beautifully crystalline acid which gave analytical values agreeing closely with those calculated for acetyltetramethylenecarboxylic acid,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}C{<}{}^{CO{\cdot}CH_3}_{CO_2H}$$

so that decomposition with elimination of carbon dioxide or the acetyl group, so characteristic of substituted acetoacetic esters, had not occurred in this case. When I told Baeyer of these results and showed him the analyses and the specimens, he thought the matter so important that he decided to communicate the results to the Bavarian Academy that same day (31st January, 1883) and not to wait for the next number of the *Berichte*, in case, as he said, someone else might be engaged in a similar series of experiments. So the paper was written forthwith in his study and Baeyer took it at once to the Academy and it was also at the same time sent to the *Berichte*, in which it appeared under the heading "Einwirkung von Trimethylenbromid auf Natracetessigäther" in the next number (p. 208).

Victor Meyer not only wrote me a charming letter but when he visited Baeyer shortly afterwards he told him how greatly interested he was in the results. No suspicion was entertained at that time that the experimental results recorded in the paper had been incorrectly interpreted, but three years later I found, quite accidentally, that the decomposition had in fact taken quite a different course from that described and it became gradually evident that no 4-carbon

ring is produced as the result of the interaction of trimethylene bromide with the sodium derivative of acetoacetic ester. During the recrystallisation of an unusually large quantity of the so-called acetyltetramethylenecarboxylic acid from boiling water, it was noticed that carbon dioxide was gradually given off and, after boiling had been continued until the evolution had ceased, no acid separated on cooling. *It was expected that the solution would now be found to contain acetyltetramethylene, but in place of this a substance was isolated which on careful investigation* proved to be acetobutyl alcohol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

There was just a possibility that this ketone alcohol might have been formed from acetyltetramethylene by the addition of water and disruption of the 4-carbon ring, but it gradually became evident that it was the interpretation of the course of the interaction of trimethylene bromide with the sodium derivative of acetoacetic ester which was at fault. It is now known that the following scheme represents what actually takes place. The bromopropylacetoacetic ester produced in the first stage yields, on treatment with sodium ethylate, the sodium derivative of the tautomeric modification, and this decomposes on heating with the formation of methyldehydrohexonecarboxylic ester:

$$\begin{array}{l} CH_3{\cdot}C(ONa){=}C{\cdot}CO_2Et \\ \quad BrCH_2{\cdot}CH_2{\cdot}CH_2 \end{array} \longrightarrow \begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}CO_2Et \\ \;O{<}CH_2{\cdot}CH_2{\cdot}CH_2 \end{array}$$

The free acid, which was thought to be acetyltetramethylenecarboxylic acid, is therefore methyldehydrohexonecarboxylic acid, *or in other words it is the carboxylic acid of the anhydride of acetobutyl alcohol and as such it decomposes on boiling with water into acetobutyl alcohol and carbon dioxide:*

$$\begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}CO_2H \\ \;O{<}CH_2{\cdot}CH_2{\cdot}CH_2 \end{array} + H_2O = \begin{array}{r} CH_3{\cdot}CO{\cdot}CH_2 \\ OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2 \end{array} + CO_2$$

In complete ignorance of the incorrect interpretation of the initial synthesis, the new method was vigorously developed in various directions and in July of 1883 a paper was published in the *Berichte* (p. 1787) containing a description of the action of trimethylene bromide on the sodium derivative of malonic ester. It was recognised that the decomposition might proceed in two directions with the formation either of tetramethylenedicarboxylic ester or of allylmalonic ester,

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2 + NaOEt \longrightarrow$$
$$CH_2{<}\begin{array}{c}CH_2\\CH_2\end{array}{>}C(CO_2Et)_2 \text{ or } CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2,$$

and the acid obtained on hydrolysis and elimination of carbon

dioxide might be either tetramethylenecarboxylic acid or allylacetic acid,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}CH{\cdot}CO_2H \text{ or } CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

Careful examination showed that the acid produced in this way was not allylacetic acid: it distilled at 193°, whereas allylacetic acid distils at 185°, and it did not, like the latter, combine with bromine or hydrobromic acid. Also the melting points and boiling points of a number of its derivatives were found to differ widely from those of the corresponding derivatives of allylacetic acid. The subsequent exhaustive examination of the acid, including the determination of the magnetic rotation, refractive index and other physical properties, entirely confirmed the view that it is tetramethylenecarboxylic acid and this view has indeed never been disputed.

This acid is, however, not the first derivative of tetramethylene to be synthesised, because in 1881 (*Annalen*, **208**, 334) Markownikoff and Krestownikoff obtained an acid, m. p. 171°, which they named tetrylenedicarboxylic acid, by the hydrolysis of the ester which is formed in small quantity when ethyl α-chloropropionate is heated with dry sodium ethylate:

$$\begin{matrix} CO_2Et{\cdot}CHCl{\cdot}CH_3 \\ CH_3{\cdot}CHCl{\cdot}CO_2Et \end{matrix} \longrightarrow \begin{matrix} CO_2Et{\cdot}CH{-}{-}CH_2 \\ CH_2{-}{-}CH{\cdot}CO_2Et \end{matrix} \longrightarrow \begin{matrix} CO_2H{\cdot}CH{-}{-}CH_2 \\ CH_2{-}{-}CH{\cdot}CO_2H. \end{matrix}$$

This acid was subsequently investigated by E. Haworth and myself (J., 1898, **73**, 330) and found to exist in *cis*- and *trans*-modifications melting at 133° and 171° and there can be no doubt that the acid obtained by the Russian chemists was, in fact, *trans*-tetramethylene-1:3-dicarboxylic acid and was the first derivative of tetramethylene to be described. It is remarkable that this observation should have called forth so little comment and that this curious decomposition was not extended to many other cases.

During the course of the experiments on the action of trimethylene bromide on the sodium derivatives of acetoacetic ester and malonic ester, a parallel series of experiments was started using, in the place of trimethylene bromide, the more readily accessible ethylene bromide and a statement to this effect was made at the end of the first paper, published in 1883, to which I have already referred. This statement brought me into conflict with Fittig, because Fittig and his pupil Roeder happened also to be working at the action of ethylene bromide on the sodium derivative of malonic ester with an object entirely different from that which prompted my

experiments. Fittig and his pupils were at that time actively engaged in the investigation of the conditions of formation and properties of lactones, a series of researches of great importance which will always be associated with the name of Fittig and with the Strassburg laboratories in which the work was carried out. It was in connexion with these lactone researches, and because I had said that I was engaged in similar work, that a short note by Fittig and Roeder appeared in the *Berichte* of 1883 (p. 372), giving a brief outline of their experiments on the action of ethylene bromide on the sodium derivative of malonic ester. They state that their expectation was that the interaction would proceed with the formation of bromoethylmalonic ester and that this, on hydrolysis, would yield butyrolactone carboxylic acid:

$$CH_2Br{\cdot}CH_2Br + CHNa(CO_2Et)_2 \longrightarrow CH_2Br{\cdot}CH_2{\cdot}CH(CO_2Et)_2$$
$$\longrightarrow \begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO_2H.\\ O\text{———}CO\end{array}$$

But instead of butyrolactone carboxylic acid they obtained a dibasic acid, m. p. 140°, which they considered was vinylmalonic acid and which they subsequently named vinaconic acid. The formation of the vinyl acid was easily explained by assuming that the bromoethylmalonic ester, first formed, lost hydrobromic acid during the treatment with sodium ethylate and subsequent hydrolysis with alcoholic potash:

$$CH_2Br{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \longrightarrow CH_2{:}CH{\cdot}CH(CO_2H)_2$$

In a paper published in the *Berichte* (p. 54) in January, 1884, I described the results of my own experiments on the action of ethylene bromide on the sodium derivative of malonic ester and interpreted the course of the change in a manner different from that suggested by Fittig. In my view the product of the interaction was trimethylenedicarboxylic ester produced according to the scheme:

$$\begin{array}{l}CH_2Br\\ CH_2Br\end{array} + Na_2C(CO_2Et)_2 = \begin{array}{l}CH_2\\ CH_2\end{array}\!\!>\!C(CO_2Et)_2 + 2NaBr.$$

On hydrolysing the ester, I obtained an acid of m. p. 140° which careful comparison showed was identical with the vinaconic acid of Fittig and Roeder, but, instead of representing this as vinylmalonic acid, I, for various reasons some of which were not published at that time, formulated this acid as trimethylenedicarboxylic acid. When this acid was heated at 210° it decomposed with loss of carbon dioxide and formation of a monobasic acid distilling at 181°, which I named trimethylenecarboxylic acid:

$$\begin{array}{l}CH_2\\ CH_2\end{array}\!\!>\!C(CO_2H)_2 \longrightarrow \begin{array}{l}CH_2\\ CH_2\end{array}\!\!>\!CH{\cdot}CO_2H + CO_2.$$

Fittig and Roeder did not publish the detailed account of their experiments until a year later (*Annalen*, 1885, **227**, 13) and in this paper Fittig discussed my view at great length and accused me, perhaps not unjustly, of not having brought forward a single argument in support of my representation of these substances as derivatives of the 3-carbon ring, trimethylene. It must be conceded that, at that time, the balance of the published evidence was in favour of the view of Fittig that the acid of m. p. 140° is vinylmalonic acid. Fittig found that, on heating, it yields along with the monobasic acid—vinylacetic acid according to his view—a not inconsiderable quantity of butyrolactone and thus the monobasic acid exhibits the well-known property of βγ-unsaturated acids of passing into γ-lactones on distillation:

$$CH_2{:}CH{\cdot}CH(CO_2H)_2 \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H \longrightarrow \underset{O\text{———}CO}{CH_2{\cdot}CH_2{\cdot}CH_2}.$$

The dibasic acid also combines with hydrobromic acid with great ease to yield γ-bromoethylmalonic acid, and this behaviour may again be said to be in favour of the unsaturated vinylmalonic acid formula.

Arguing from analogy, the unsaturated vinylmalonic acid should also combine readily with bromine to yield βγ-dibromoethylmalonic acid, but this was found not to be the case. Fittig himself expressed his surprise that not only does the dibasic acid not react with bromine but, what is still more remarkable, the solution of the monobasic acid in chloroform may be left in contact with bromine for days without any visible decolorisation. This is a very different behaviour from that exhibited by allylmalonic acid or by the crotonic acids, all of which rapidly decolorise bromine. As you may imagine, the determination of the constitution of these acids proved, in those days, to be a very difficult matter and it was particularly unfortunate that the bromine atom in vinyl bromide, $CH_2{:}CHBr$, is so tightly bound that this substance will not react with the sodium derivative of malonic ester, otherwise this synthesis of vinylmalonic ester would clearly have settled the matter once for all. To cut a long story short, I may say that the proof that these acids are not unsaturated but are derivatives of the 3-carbon ring trimethylene was subsequently obtained in the following manner. If the two suggested formulæ for the product of the action of ethylene bromide on the sodium derivative of malonic ester, namely,

$$\text{(i) } CH_2{:}CH{\cdot}CH(CO_2Et)_2 \text{ and (ii) } \begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>\!C(CO_2Et)_2,$$

are examined it will be recognised that the former is a monosubstitution derivative, whereas the latter is a disubstitution

derivative, of malonic ester: the former may be compared with ethylmalonic ester and the latter with dimethylmalonic ester. *The ester (i) still has a hydrogen atom replaceable by sodium and should therefore react with sodium ethylate and benzyl chloride to yield* benzylvinylmalonic ester, $CH_2{:}CH{\cdot}C(C_7H_7)(CO_2Et)_2$, *whereas the ester (ii) does not contain a hydrogen atom replaceable by* sodium and cannot therefore yield a benzyl substitution derivative. When the experiment was made, it was found that, not only was no benzyl derivative produced, but that almost the whole of the original ester was recovered unchanged. This behaviour is clearly strong evidence in favour of the constitution (ii).

Just at that time an important piece of work was carried out by the Belgian chemist, Franchimont, who showed that monosubstituted malonic acids react with nitric acid in the cold with loss of two molecules of carbon dioxide, whereas disubstituted malonic acids are unchanged by this treatment. Professor Franchimont was good enough to try this interesting experiment with some of the dibasic acid, m. p. 140°, which I sent him and he reported that it did not react with nitric acid and therefore behaved as a disubstituted malonic acid. A very pure specimen of the ethyl ester of the acid of m. p. 140° was then prepared from the silver salt by the action of ethyl iodide and its magnetic rotation and refractive index were determined; the values obtained showed very clearly that the ester and therefore the acid could not be unsaturated.

Ultimately, in 1899, vinylacetic acid was prepared by J. Wislicenus (*Ber.*, **32**, 2047) and by Fichter and Krafft (*ibid.*, p. 2799) from β-hydroxyglutaric acid by distillation,

$$CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H + CO_2 + H_2O,$$

and in 1903 by Houben (*Ber.*, **36**, 2897) from the magnesium derivative of allyl bromide by decomposition with carbon dioxide:

$$CH_2{:}CH{\cdot}CH_2{\cdot}MgBr \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$$

The acid obtained by either process distils at 168° and combines immediately with bromine; it therefore has properties quite different from those of the acid obtained by Fittig and by myself by heating the acid of m. p. 140°, since this distils at 181° and is so remarkably stable to bromine. It is clear, therefore, that the synthesis of vinylacetic acid supplies the final proof that the acid, b. p. 181°, must be regarded as trimethylenecarboxylic acid, and that the acid, m. p. 140°, is trimethylenedicarboxylic acid.

Although the synthesis of trimethylenecarboxylic acid in 1883 was the first occasion on which a derivative of trimethylene had been

obtained in a pure state, it cannot be described as the first synthesis of the 3-carbon ring, because Freund, in 1882 (*Monatsh.*, **3**, 625), had treated trimethylene bromide with sodium and obtained a gas which was subsequently shown to contain trimethylene mixed with much propane and propylene. In 1887, Gustavson (*J. pr. Chem.*, [2], **36**, 300) greatly improved the method of preparation by substituting zinc and alcohol for sodium, but the gas was again contaminated with propane and probably with hydrogen. Lastly, in 1907, Willstätter (*Ber.*, **40**, 4459), employing also the action of zinc on an alcoholic solution of trimethylene bromide, but greatly improving the conditions and then liquefying the gas, succeeded in isolating trimethylene in a pure state. Trimethylene boils at about −35° and when heated, especially in contact with a catalyst such as alumina, readily undergoes isomerisation into propylene.

The interval between the Fatty and the Aromatic Series had now been considerably lessened by the synthesis and examination of the trimethylene- and tetramethylene-carboxylic acids and the next step was to devise some method for the preparation of a derivative of the 5-carbon ring. There seemed every reason to believe that pentamethylenecarboxylic acid might be readily obtained by making use of the method which had been so successful in the previous cases, namely, by acting on the sodium derivative of malonic ester with tetramethylene bromide:

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + CNa_2(CO_2Et)_2 \longrightarrow \begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!C(CO_2Et)_2 \longrightarrow \begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!CH{\cdot}CO_2H.$$

Unfortunately, at that time tetramethylene bromide was unknown and it was not until 1894 or 10 years later (J., 1894, **65**, 86) that it was obtained accidentally by a process which for a long time was not understood. The attempt was being made to convert trimethylene bromide into the dicyanide, then into pentamethylenediamine by reduction, then into the glycol by nitrous acid, and then into pentamethylene bromide by treatment with hydrobromic acid,

$$CH_2Br{\cdot}CH_2{\cdot}CH_2Br \qquad CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$$
$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$
$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \qquad CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br,$$

with the object of using the dibromide for the synthesis of hexamethylenecarboxylic acid by the usual method. But the substance actually obtained as the result of this series of changes was found to be a mixture of pentamethylene bromide with a good deal of a lower-boiling bromide and, on very careful fractionation, this proved

to be tetramethylene bromide, one CH_2-group having in some way been lost during its formation. The solution of the mystery may be taken to be the following: The strongly alkaline potassium cyanide which was in common use in those days, evidently acted as if it were a mixture of cyanide and hydroxide and led to the formation of a good deal of hydroxy-propyl cyanide. When this was reduced and then treated with nitrous acid and then with hydrobromic acid, tetramethylene bromide, the substance for which we had so long searched in vain, was produced:

$$CH_2Br{\cdot}CH_2{\cdot}CH_2Br \qquad OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$$

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \qquad CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$$

When the sodium derivative of malonic ester was digested with this new dibromide, pentamethylenedicarboxylic ester was produced in almost quantitative yield, and this, on hydrolysis and elimination of carbon dioxide, supplied the long-sought-for pentamethylenecarboxylic acid, a substance characterised by great stability. Thus the gap between the fatty and the aromatic series had now been bridged by the synthesis of the following acids:

Trimethylenecarboxylic acid, $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!CH{\cdot}CO_2H$, b. p. 181°.

Tetramethylenecarboxylic acid, $\begin{matrix}CH_2-CH_2\\ |\qquad\quad |\\ CH_2-CH{\cdot}CO_2H\end{matrix}$, b. p. 195°.

Pentamethylenecarboxylic acid, $\begin{matrix}CH_2-CH_2\\ |\\ CH_2-CH_2\end{matrix}\!\!>\!CH{\cdot}CO_2H$, b. p. 215°.

Finally the pentamethylene bromide, obtained in the way I have just described, was purified by careful fractionation and caused to interact with the sodium derivative of malonic ester, and this led to the synthesis of hexamethylenecarboxylic acid (b. p. 232°), which proved to be identical with the hexahydrobenzoic acid resulting from the reduction of benzoic acid.

I have already mentioned that the synthesis of pentamethylenecarboxylic acid had to be postponed over and over again because of the impossibility of obtaining tetramethylene bromide and that the acid was actually not prepared until 1894. In view of this difficulty, another method had to be devised for the synthesis of the 5-carbon ring, and this ring was produced for the first time in 1885 or nearly 10 years before the date of the synthesis of pentamethylenecarboxylic acid. It had been noticed from the first that when ethylene bromide or trimethylene bromide interacts with the sodium derivative of malonic ester, there are always formed, along with the trimethylene- or tetramethylene-dicarboxylic esters, small quantities of high-

boiling substances, and these were found to be derived from two molecules of malonic ester. Thus, in the cases just mentioned, these secondary products are butanetetracarboxylic ester and pentanetetracarboxylic ester, $(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$ and $(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$. On account of the fact that these substances readily *yield disodium derivatives*, they have proved to be of considerable value for ordinary synthetical purposes. But of much more interest is the fact that they serve as valuable and convenient starting points for the synthesis of closed-chain derivatives, and their use has made possible, as I will presently show, the preparation of a great variety of interesting and important substances which could hardly have been obtained by any other method.

Pentanetetracarboxylic ester was the starting point in the first synthesis of the pentamethylene ring, a synthesis which was carried out in the autumn of 1885 and published in December of that year (*Ber.*, **18**, 3246). When the disodium derivative of this ester was treated with bromine, ring closure occurred, and the pentamethylenetetracarboxylic ester obtained, in almost quantitative amount, yielded on hydrolysis and elimination of carbon dioxide pentamethylene-1 : 2-dicarboxylic acid,

$$CH_2\left<\begin{matrix}CH_2\cdot CNa(CO_2Et)_2\\ CH_2\cdot CNa(CO_2Et)_2\end{matrix}\right. + 2Br \longrightarrow CH_2\left<\begin{matrix}CH_2-C(CO_2Et)_2\\ \quad\quad\;\; | \\ CH_2-C(CO_2Et)_2\end{matrix}\right.$$

$$\longrightarrow CH_2\left<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ \quad\quad\;\; | \\ CH_2\cdot CH\cdot CO_2H\end{matrix}\right.$$

an acid which was later shown to exist in well-defined *cis*- and *trans*-modifications. *This was the first synthesis of the 5-carbon ring.*

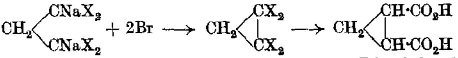
The fact that the formation of the 5-carbon ring takes place so readily and that the pentamethylenedicarboxylic acid obtained in this way should prove to be a substance of such marked, it might even be said unusual, stability excited a great deal of interest at the time.

During 1885, Baeyer was gradually working out his "Spannungs Theorie," a conception which was destined to exert so profound an influence on the whole subject of ring closure. I remember that on two occasions he invited me into his study and explained to me, with the aid of models which had been specially made, his views on the stability and ease of formation of rings based on the tetrahedral configuration of the carbon atom, and these views gradually gave rise to the "Spannungs Theorie." This remarkable theory, published in August, 1885 (*Ber.*, **18**, 2278), occupies only two pages of print and its description always seems to me to be a striking example of how much can be said in a very small space.

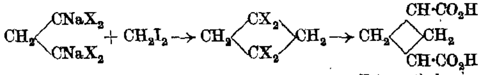
As is well known, one of the consequences of the theory is that the 5-carbon ring should prove to be the most stable and most easily formed of all rings or, as Baeyer himself puts it, "pentamethylene should be the most stable configuration and should be formed rather more easily than hexamethylene."

In discussing this point with me, Baeyer remarked that it was unfortunate that no pentamethylene derivative had so far been prepared so as to make the direct comparison possible. It is therefore not difficult to picture how greatly interested Baeyer was when a short time after the publication of his theory the synthesis of pentamethylene-1 : 2-dicarboxylic acid, which I have just described, actually demonstrated not only that the 5-carbon ring is produced with great ease but that it is also characterised by great stability. He considered that this synthesis confirmed in a very welcome manner the views which he had so shortly before developed in his "Spannungs Theorie."

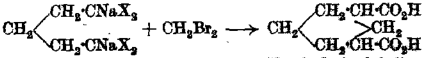
The method which had been used so successfully in the synthesis of the pentamethylene ring was now developed in a great many directions and it was found that substances of the type $(CO_2Et)_2CH\cdot[CH_2]_n\cdot CH(CO_2Et)_2$ lend themselves so readily to so great a variety of ring syntheses that they may perhaps be said to be the most valuable reagents we possess for this purpose. Although much of the synthetical work carried out with the aid of substances of this kind dates from before 1894 and may thus claim to be included in an account of the Early History of Ring Closure, it would take me far too long to go into this matter in any detail. I venture, however, to introduce a short table which gives in a general way some idea of the scope of these synthetical methods and includes one or two of the more interesting special cases ($X = CO_2Et$).

(i) 

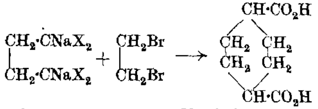
Trimethylene-1 : 2-dicarboxylic acid.

(ii) 

Tetramethylene-1 : 3-dicarboxylic acid.

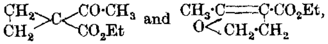
(iii) 

Hexahydroisophthalic acid.

(iv) 

Hexahydroterephthalic acid.

The last syntheses to which I will refer, because they are perhaps in many ways as novel and interesting as any of those I have already mentioned, are the syntheses of derivatives of hydrindonaphthene (hydrindene) and of tetrahydronaphthalene published by Baeyer conjointly with myself in the *Berichte* of January and February, 1884 (pp. 122 and 448). I pointed out earlier in this lecture that when trimethylene bromide interacts with the sodium derivative of acetoacetic ester, the process follows an unexpected course leading to the formation of methyldehydrohexonecarboxylic ester instead of acetyltetramethylenecarboxylic ester as had been expected. When, in an analogous series of experiments, commenced at the same time, the trimethylene bromide was replaced by ethylene bromide, a mixture of esters was obtained which could not at first be separated into its constituents and it was not until much later that it was possible to show that this product consists essentially of acetyltrimethylenecarboxylic ester mixed with varying quantities of methyldehydropentonecarboxylic ester,

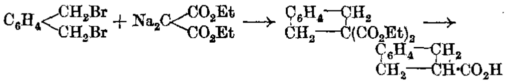


the process in this case having taken place in the two possible directions.

The main difficulty was that it was not found possible to isolate any of the products in a crystalline condition, and it occurred to me that, if I replaced, in the interaction with the sodium derivative of acetoacetic ester, the ethylene bromide by phenylethylene bromide, $C_6H_5 \cdot CHBr \cdot CH_2Br$, the esters produced or more probably the corresponding acids might be crystalline and therefore lend themselves more readily to separation.

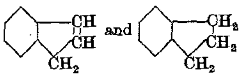
When I mentioned this idea to Baeyer, I thought that he did not at the time seem to be interested, but a few days afterwards he told me that, in thinking the matter over, a modification of the idea had suggested itself to him which he thought might lead to results of considerable interest and importance. If, he said, instead of phenylethylene bromide, the then unknown isomeric bromide, *o*-xylylene bromide, $C_6H_4(CH_2Br)_2$, could be prepared, it might react with malonic ester to yield derivatives of hydrindonaphthene

(hydrindene) and he proceeded to sketch out the scheme exactly as he wrote it later for publication in the *Berichte*:



He told me that he had long wished to synthesise indene, or indonaphthene as he then called it, and examine its properties mainly because of its relationship to indole and to the whole indigo group, the investigation of which had occupied him for so many years. It was most fortunate that *o*-xylene could be obtained at that time in almost pure condition from the firm of Langenfeld and Reuter, but Baeyer was very doubtful whether, on bromination at the boiling point, this would yield *o*-xylylene bromide in anything like a pure condition. He rather expected that the product would contain considerable quantities of the isomeride, $C_6H_4(CHBr_2)\cdot CH_3$, as well as of substances containing bromine substituted in the benzene ring. A mixture is indeed formed under these conditions, but *o*-xylylene bromide has fortunately so great a facility for crystallising that there is not much difficulty in preparing it in a pure condition. The main trouble proved to be the effect of this substance on the eyes, which was much more severe than had been anticipated.

The interaction between *o*-xylylene bromide and malonic ester proceeded exactly as Baeyer had predicted and the hydrindonaphthenedicarboxylic ester so obtained yielded, on hydrolysis and elimination of carbon dioxide, hydrindonaphthenecarboxylic acid. It was shown at a later date (1894) that the barium salt of this acid is decomposed on heating with separation of indonaphthene (indene), and since this on reduction yields hydrindonaphthene (hydrindene),



the synthesis of both these important hydrocarbons was accomplished in this way.

The next step was to extend these methods to the hexahydronaphthalene series and this was done in two different ways both of which led ultimately to the same result. In the first process *o*-xylylene bromide and the disodium derivative of acetylenetetracarboxylic ester were heated with alcohol in a sealed tube and the product was hydrolysed; an acid was then obtained which, on

heating at 185°, decomposed with elimination of carbon dioxide and formation of tetrahydronaphthalenedicarboxylic acid:

$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + \begin{matrix}NaC(CO_2Et)_2\\NaC(CO_2Et)_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2-C(CO_2Et)_2\\CH_2-C(CO_2Et)_2\end{matrix} \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2-CH\cdot CO_2H\\CH_2-CH\cdot CO_2H\end{matrix}$$

The still more interesting second process consisted in boiling an alcoholic solution of the sodium derivative of chloromalonic ester with xylylene bromide; rather unexpectedly, the following process then took place almost quantitatively:

$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + \begin{matrix}NaCCl(CO_2Et)_2\\NaCCl(CO_2Et)_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CCl(CO_2Et)_2\\CH_2\cdot CCl(CO_2Et)_2\end{matrix}$$

There was of course always the possibility that the sodium derivative of chloromalonic ester would interact with itself with the formation of the substance $(CO_2Et)_2C{:}C(CO_2Et)_2$, but the bromine atoms in *o*-xylylene bromide proved to be more reactive than the chlorine atom in chloromalonic ester, so that the process proceeded almost entirely in the direction I have indicated. When *o*-xylylenedichlorodimalonic ester is reduced by zinc dust, it yields *o*-xylylenedimalonic ester, the disodium derivative of which is readily acted on by iodine with closure of the ring, and the ester produced is identical with the tetrahydronaphthalenetetracarboxylic ester obtained with the aid of acetylenetetracarboxylic ester in the way I have just described.

$$C_6H_4{<}\begin{matrix}CH_2\cdot CH(CO_2Et)_2\\CH_2\cdot CH(CO_2Et)_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CNa(CO_2Et)_2\\CH_2\cdot CNa(CO_2Et)_2\end{matrix} \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2-C(CO_2Et)_2\\CH_2-C(CO_2Et)_2\end{matrix}$$

The last step in this investigation consisted in heating the silver salt of tetrahydronaphthalenedicarboxylic acid in a test-tube; decomposition took place readily with sublimation of naphthalene. This process constitutes one of the best-known syntheses of naphthalene.

It is not my intention to develop this brief sketch any further, but I think I may say that the importance which Baeyer attached to the methods I have been describing (compare *Ber.*, 1884, **17**, 122) has been fully justified by the wide subsequent development of the Chemistry of the Closed Carbon Chains.

CLXXVII.—*The Effect of Gases on the Colour of Iodine Vapour, and the Solvent Action of Various Vapours on Solid Iodine.*

By Robert Wright and Thomas McGregor.

Dewar (P., 1898, 241) observed that the colour of iodine vapour was less dense in a vacuous flask than in one at the same temperature containing air, and that the colour in the latter case was more purple than in the former. It was suggested that this increase in depth of colour might be due to a greater volatility of iodine in air than in a vacuum, and Dewar's observation has been frequently cited as an example of the solubility of a solid in a gas under ordinary conditions of temperature and pressure.

A repetition of Dewar's experiment was carried out. Iodine was sealed in a vacuous bulb and heated in water to about 90°; the tip of the bulb was then broken. With the inrush of air the colour of the vapour at once deepened and became more purple. With a second bulb, containing *less iodine than would saturate the available space with vapour at the temperature of the experiment,* the same effect was observed; in this case, since no excess of solid was present, the effect cannot be attributed to the solubility of iodine in air.

A qualitative spectroscopic examination of the effect was also made. A small quantity of iodine was placed in a Lilburn flask, which was then evacuated to a pressure of about 1 mm. and sealed off. The sealed flask was held concentrically in a large beaker of water placed in front of the slit of a Hilger photographic spectroscope. The water was heated to 90° and a beam of light from a Point-o-lite lamp focused on the slit. Comparative photographs were then taken on a panchromatic plate, first with the iodine alone in the vacuous flask and then, at the same temperature, in the presence of air, the flask being opened and resealed between the exposures. The results showed an increase of absorption in the second case, the head of the absorption band in the green having moved towards the red end of the spectrum. The same effect was observed when less iodine was used than would saturate the available space with vapour at the temperature of the experiment. A further series of photographs was then taken in experiments in which the air was replaced by nitrogen, oxygen, carbon dioxide, and argon, and in all cases the same result was obtained. In order to compare more accurately the effect of the different gases, a small amount of iodine was placed in a 20 cm. polarimeter tube fitted with two side tubes; this was then placed in a glass-sided thermostat at 50° and arranged in front of the spectroscope. A series of four photographs

PLATE I.

Air and vacuum.
Excess of I_2.

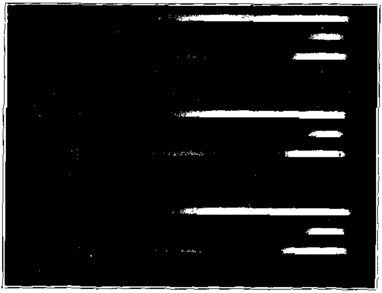


PLATE II.

Argon and vacuum.
Excess of I_2

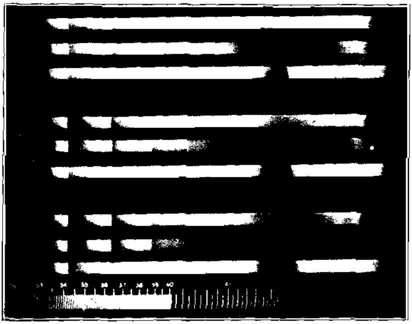
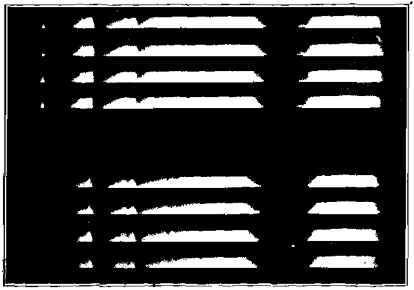


PLATE III.

Spectra of I_2 apour in air, itrogen, oxygen nd CO_2.

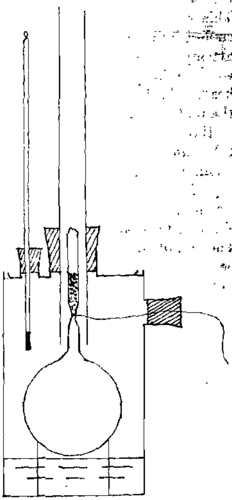


[*To face page* 1365.]

was taken in which the gas in the tube was successively air, nitrogen, oxygen, and carbon dioxide. The spectra were identical in all four cases, and this would seem to indicate that the colour change is not due to the solubility of the iodine in the gas used or to chemical action between the gas and the iodine vapour, but possibly to the effect of pressure on the iodine vapour.

In the accompanying photographs, Plate I shows three sets (with different exposures) of iodine absorption spectra in air and in a vacuum, with a comparison continuous spectrum in each case; Plate II shows three similar sets in argon and in a vacuum; and *Plate III shows two sets taken in* the 20 cm. tube with the four gases air, nitrogen, oxygen, and carbon dioxide.

FIG. 1.



It was thought of interest to try to determine the relative volatility of iodine in air and in a vacuum at 100° by measuring directly the quantity of iodine which would saturate a definite space with vapour under the two conditions. About 0·5 g. of iodine was placed in a flask of 130 c.c. capacity, the flask was sealed off, and while still hot the iodine was shaken into the neck, where it melted and adhered to the glass close to the sealed tip. (Under suitable conditions, only a small amount of iodine will sublime into the body of the flask, but if this amount is excessive it may be driven back by a prolonged heating of the bulb and cooling of the neck.) The flask was now placed in the steam-bath shown in Fig. 1 and heated at 100°. The steam-bath was constructed from a large lever-lidded paint tin fitted with a thermometer and a long brass tube to act as an air-condenser, the upper end of the condenser was attached to a large bottle and a manometer so that the pressure inside the vessel might be regulated and the temperature kept at 100°. After 5—7 hours' heating, the flask was removed from the bath and cooled quickly in a stream of water;

the iodine vapour condensed on the walls and, as diffusion of the vapour in air is slow, during the cooling hardly any iodine sublimed from the solid in the neck of the flask. The flask was now cut open, the amount of iodine in the bulb determined by titration with $N/50$-thiosulphate, and the volume of the flask measured by filling with water. For three consecutive determinations the quantity of iodine in 100 c.c. was found to be practically constant (see table).

When the same method was used with iodine in a vacuous flask the results obtained were much higher and were not constant. This was due to the sublimation of iodine from the neck into the cooling bulb during the removal of the flask from the bath. Various attempts were made to correct this and the most satisfactory result was obtained by breaking the neck of the flask while still in the heating bath, so that all sublimation due to the quicker cooling of the bulb was avoided. For this purpose a slight modification of the method was necessary. The neck of the flask was made of 5 mm. tube and a constriction was made about 3 cm. from the bulb; 3 cm. above the constriction there was a plug of glass wool, on the top of which were placed the fragments of iodine. The apparatus was now evacuated and sealed off. A loop of string was fastened to the constriction, and the flask placed in position in the heater. The end of the brass condenser tube was pushed well down over the neck of the flask past the constriction, the string passing through a slot cut in the end of the brass tube and then through a stopper in the wall of the heater. A period of 2 hours' heating was usually sufficient for the evacuated flask; the string was then pulled strongly, drawing the neck of the flask against the condenser tube until the former fractured. Steam entered the bulb and the broken end fell into the water of the heater. The bulb was now removed from the heater and its iodine content and volume were determined as before. The results for three consecutive estimations are shown in comparison with those obtained for air. They are not quite so regular but are always slightly higher, so there is no indication of iodine being soluble in air. The values for the vapour pressure of iodine at 100° are inserted in the table and are calculated on the assumption that iodine vapour obeys the gas laws and that the gram-molecular volume is 22·4 litres at N.T.P.

Weight (g.) of saturated iodine vapour in 100 c.c. at 100°.

	a.	*b*.	*c*.	Average.	V.p. (mm.).
In air	0·05032	0·05025	0·05060	0·05039	46·2
In a vacuum	0·05171	0·05182	0·05227	0·05193	47·5

A number of measurements were carried out to determine whether iodine is soluble in the vapours of those solvents in which, as liquids,

it dissolves easily. The solvent vapours employed were benzene, toluene, alcohol, ether, carbon tetrachloride, and chloroform. The method and apparatus have already been described by one of us (J., 1915, **107**, 1527) for the determination of the vapour pressure of solid iodine. Purified air was first passed, at room temperature, through a weighed bubbler containing the solvent under investigation. The air and vapour then passed over iodine heated at 100° and the iodine carried over by the mixed gases was estimated. The volume occupied by the solvent vapour at 100° was calculated by application of the gas laws from the weight of solvent used, and the volume of air was measured after the removal of the solvent vapour by a suitable absorbent. The total amount of iodine carried over, less the amount due to the air alone, gives the quantity of iodine carried by the solvent vapour.

Although the quantity of iodine carried over by a litre of air at 100° was found by repeated estimations to be perfectly definite, no constant results could be obtained for the vaponrs. It was not infrequently found that, using the same iodine for a series of determinations, a litre of solvent vapour would carry over more iodine than a litre of air during the earlier determinations of the series, but this quantity would decrease in the later estimations and might even apparently become negative, *i.e.*, less iodine would be carried over by the mixture of air and solvent vapour than would be obtained by the air constituent of the mixture acting alone.

After prolonged exposure to the air–vapour mixture, the surface of the iodine frequently became moist, and in some cases the whole of the iodine melted. It would thus seem that the iodine was absorbing some of the solvent vapour and forming a solution which would of necessity have a lower iodine vapour pressure than the pure iodine, and this effect would mask any solvent action in the vapour phase. The positive results in the first determinations of a series were obtained before much of the vapour had been absorbed on the surface of the iodine.

Perman (J., 1903, **83**, 1168) found that the partial pressure of water vapour over aqueous ammonia was less than that of pure water; for although water vapour may be very soluble in ammonia gas, the presence of ammonia in the liquid phase lowers the water vapour pressure to such an extent that any solubility in the vapour phase is more than counterbalanced. It may, however, be suggested that solubility in the vapour phase is a factor in those positive deviations from the mixture rule which are sometimes obtained for the vapour pressures of binary liquid mixtures.

GLASGOW UNIVERSITY. [*Received, April 3rd, 1929.*]

CLXXVIII.—*The Chemistry of the Caryophyllene Series. Part II. Clovene and* iso*Clovene.*

By George Gerald Henderson, Robert Osborne Orr McCrone, and John Monteath Robertson.

Wallach and Walker (*Annalen*, 1892, **271**, 283) showed that when caryophyllene alcohol is heated with phosphoric oxide caryophyllene is not regenerated but instead the tricyclic sesquiterpene clovene is produced. We have now ascertained that when other methods of dehydrating the alcohol, *e.g.*, heating with anhydrous oxalic acid, are employed, the result is the same; in no case has caryophyllene been obtained. Moreover, the liquid hydrocarbon which is formed as a by-product when caryophyllene is hydrated by Wallach and Walker's method is closely similar to, if not identical with, clovene. Caryophyllene can be regenerated from its crystalline dihydrochloride by treatment of the latter with a saturated methyl-alcoholic solution of potassium hydroxide or with a concentrated solution of sodium methoxide (Semmler and Mayer, *Ber.*, 1910, **43**, 3451), but when the dihydrochloride is heated with dilute alcoholic alkalis, or with sodium acetate and acetic acid, or with pyridine or quinoline, the product is again a liquid tricyclic sesquiterpene instead of dicyclic caryophyllene. Further a liquid by-product is obtained in varying quantities during the preparation of caryophyllene dihydrochloride, and we have found that this liquid is capable of dissolving the dihydrochloride, which i not completely separated even if the solution is strongly cooled. A the same time, when allowance is made for the quantity of th dihydrochloride retained in solution after cooling, analysis indicate that the liquid is largely composed of a rather unstable monc hydrochloride of a sesquiterpene. The hydrocarbon regenerate from this liquid by the usual methods and purified by fractional di tillation closely resembles clovene in its physical properties and i the fact that it does not yield a crystalline hydrochloride, as is al the case with the sesquiterpene obtained as a by-product in tl hydration of caryophyllene. The physical constants of the hydrocarbons are as follows:

(1) B. p. 111—113°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·924, $n_D^{20^\circ}$ 1·4980, $[R_L]_D$ 64·7.
(2) B. p. 110—114°/10 mm., $d_{4^\circ}^{17^\circ}$ 0·933, $n_D^{17^\circ}$ 1·5020, $[R_L]_D$ 64·5.
(3) B. p. 110—114°/9 mm., $d_{4^\circ}^{10^\circ}$ 0·926, $n_D^{10^\circ}$ 1·5010, $[R_L]_D$ 64·8.

(1) Clovene, (2) sesquiterpene obtained by heating caryophylle dihydrochloride with quinoline, (3) sesquiterpene obtained in hy ation of caryophyllene: $[R_L]_D$ calculated for tricyclic sesquiterpe 64·4. It is evident that under the influence of mineral acids a

some other reagents, caryophyllene readily undergoes ring closure with formation of clovene or of another tricyclic sesquiterpene which is very similar to clovene in its physical properties.

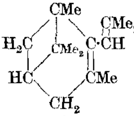
Clovene is attacked by potassium permanganate, but so far no definite oxidation products have been isolated, and all attempts to prepare an alcohol from it by hydration have been unsuccessful. It does not appear to yield either eudalene or cadalene when heated with sulphur, and therefore does not belong to either the eudesmene or the cadinene group of sesquiterpenes.

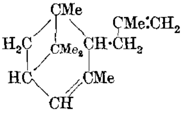
We have recently discovered that modification of the conditions under which Wallach and Walker's method of dehydrating caryophyllene alcohol is carried out results in the production of a mixture of clovene and another tricyclic sesquiterpene, which can be separated by fractional distillation. The new sesquiterpene, for which we propose the name iso*clovene*, is a colourless, somewhat viscous liquid, b. p. 130—131°/12 mm., $d_{4^{\circ}}^{19^{\circ}}$ 0·943, $n_{D}^{19^{\circ}}$ 1·5039, $[\alpha]_{D}^{14^{\circ}}$ −56·6°, $[R_L]_D$ 64·11. It is characterised by the formation of a crystalline *monohydrochloride*, $C_{15}H_{25}Cl$, m. p. 87°, and *monohydrobromide*, $C_{15}H_{25}Br$, m. p. 75°, from which the hydrocarbon may be regenerated in a pure state. These compounds are quite different from the remarkably stable substances of the same composition which are obtained by the action of phosphorus pentachloride and pentabromide on caryophyllene alcohol, which melt at 62° and 63°. *iso*Clovene is much more unstable than clovene, resinifying quickly when exposed to air and becoming sticky and resinous even when enclosed. When heated to its boiling point with phosphoric oxide, it is completely decomposed, and thus the possibility of obtaining it from caryophyllene alcohol might easily escape notice. It unites with 1 mol. of bromine, but the dibromide is also very unstable.

On treatment of a solution of *iso*clovene hydrochloride in glacial acetic acid with silver acetate a good yield of the acetate of *iso*clovene alcohol was obtained. The *alcohol*, $C_{15}H_{25}\cdot OH$, purified by recrystallisation from ethyl acetate, is a colourless crystalline solid, m. p. 98°, $[\alpha]_{D}^{20^{\circ}} = 227°$. It is saturated towards bromine, and presumably tertiary, because attempts to prepare esters were unsuccessful, the alcohol undergoing dehydration in the process; it does not react with phenylcarbimide. The melting point lies near to that of caryophyllene alcohol, but a mixture of the two melts about 20° lower; it is also more sparingly soluble in alcohol and in ethyl acetate than caryophyllene alcohol.

The formulæ suggested by Semmler for β- and γ-caryophyllene (I and II) have been criticised on the ground that they are not in conformity with the now generally accepted view that the carbon nuclei of sesquiterpenes are built up of three isoprene nuclei.

Moreover, as Deussen has pointed out (*J. pr. Chem.*, 1926, **114**, 63), neither hydrocarbon yields a dihydro-compound on treatment with sodium and alcohol, and therefore presumably neither contains a conjugated double linkage. In a later paper (*J. pr. Chem.*, 1927, **117**, 273) Deussen suggests formula (III) for γ-caryophyllene, in consideration of the fact that he obtained succinic acid, along with other products, by the action of steam on its ozonide. If this is the constitution of γ-caryophyllene, formula (IV) may be tentatively assigned to β-caryophyllene alcohol (compare Henderson, Robertson, and Kerr, J., 1926, 62) and formula (V) to clovene. The relation of *iso*clovene to clovene remains for the present unsettled.


(I.)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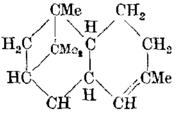
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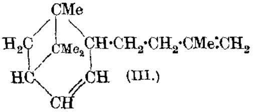
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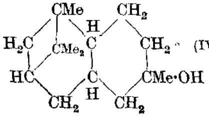

(IV.)

EXPERIMENTAL.

Preparation of β-Caryophyllene Alcohol and its Dehydration Products.—Caryophyllene was repeatedly distilled at 13 mm. pressure, and four fractions, b. p. 109—115°, 115—120°, 120—123°, and 123—127°, were collected. Each fraction was hydrated by tht method of Asahina and Tsukamoto (*J. Pharm. Soc. Japan*, 1922 463), which yields the α- as well as the β-alcohol; there was very little difference in the quantities of the latter obtained from the several fractions. 100 C.c. of caryophyllene were added drop by drop to a mixture of 80 c.c. of absolute ether and 30 c.c. of sulphuric acid monohydrate cooled to 0°, the temperature of the reaction mixture being maintained below 10°. After the reaction mixtur (kept in the cooling mixture) had reached room temperature, it wa poured into a mixture of ice and sodium carbonate, and the alkalin liquid distilled in steam until nothing more passed over. The firs portion of the distillate consisted mainly of a hydrocarbon : fror the other portion the β-alcohol crystallised on cooling; it wa redistilled in steam and crystallised from acetone until its meltin

point was 96°. 90 G. of phosphoric oxide were added in small portions to 70 g. of the alcohol heated to its melting point. The vigorous reaction was controlled by cooling and, when completed, the product was neutralised with sodium carbonate and distilled in steam. The oily liquid which passed over was extracted and dried (with anhydrous sodium sulphate) in ether and then distilled several times under diminished pressure. Two fractions were obtained: (1) a *mobile oil*, b. p. 111—113°/10 mm., which proved to be clovene, and (2) a slightly more viscous oil, b. p. 115—118°/10 mm. The latter was dissolved in twice its volume of absolute ether, cooled to 0°, and slowly saturated with hydrogen chloride. After standing for 3 days at that temperature, the ether was evaporated under diminished pressure and the dark oily residue cooled to −60°, with constant stirring. After some time the *monohydrochloride* of *iso*clovene solidified; after draining on a porous plate, it crystallised from ethyl acetate in hard colourless needles, m. p. 87° (Found: C, 74·6; H, 10·4; Cl, 14·6. $C_{15}H_{25}Cl$ requires C, 74·8; H, 10·5; Cl, 14·7%). Unlike the parent hydrocarbon, this is a stable compound when pure. The *monohydrobromide* of *iso*clovene was prepared in a similar manner. It begins to crystallise from the cooled ethereal solution as saturation approaches, and when purified by recrystallisation from ethyl acetate forms colourless prisms, m. p. 75°. When impure it is apt to decompose on exposure to moist air (Found: Br, 28·2. $C_{15}H_{25}Br$ requires Br, 28·2%).

The fraction of lower boiling point (111—113°/10 mm.) obtained along with *iso*clovene by the dehydration of caryophyllene alcohol as described above was treated in a similar manner with hydrogen chloride, but only a trace of the solid hydrochloride was formed. The great bulk of the product was a dark liquid, which after standing over soda-lime in a vacuum desiccator was found to contain 9·3% of chlorine. A similar liquid was obtained when the hydrocarbon formed as a by-product in the hydration of caryophyllene was purified by distillation over sodium and treated as above with hydrogen chloride.

In another experiment β-caryophyllene alcohol was dehydrated according to Wallach and Walker's method by treatment with phosphoric oxide at its boiling point and heating the liquid thus obtained a second time with the pentoxide. The final product in this case consisted solely of clovene, b. p. 110—113°/10 mm., and gave no crystalline hydrochloride. This result was to be expected, because we have found that *iso*clovene is completely decomposed when heated with phosphoric oxide even at temperatures below its boiling point.

Pure *isoclovene* was obtained from the monohydrochloride as

follows: 3 g. of the hydrochloride and 3·5 g. of anhydrous sodium acetate were boiled under reflux with 25 c.c. of glacial acetic acid for 4 hours; the acid was then neutralised with sodium carbonate, the product extracted with ether, and the ethereal solution washed and dried. After evaporation of the ether the liquid which remained was distilled over sodium under diminished pressure, and *iso*clovene finally obtained as a colourless, somewhat viscous liquid, with the physical constants quoted above (Found: C, 87·8; H, 11·7 $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). When a solution of the hydrocarbon in two volumes of anhydrous ether is treated with hydrogen chloride and then concentrated, a quantitative yield of *iso*clovene monohydrochloride separates quickly.

Preparation of iso*Clovene Alcohol.*—10·5 G. of silver acetate were added to a solution of 15 g. of *iso*clovene hydrochloride in 200 c.c. of glacial acetic acid, and the mixture was agitated in the dark for 4 days. After dilution with ice-water the acid was neutralised with sodium carbonate, and the crude ester extracted with light petroleum. The solution was dried over anhydrous sodium sulphate, the solvent distilled off, and the oily residne mixed with a little ethyl acetate and strongly cooled; about 10 g. of the ester then crystallised. When recrystallised from ethyl acetate it was quite colourless and melted at 25—26°. It was hydrolysed by warming with methyl-alcoholic potassium hydroxide, and also by leaving a solution in ethyl acetate exposed to moist air for some weeks; the *alcohol* then slowly separated. After several crystallisations from ethyl acetate the alcohol melted sharply at 98°. It is optically active: $\alpha_D^{?} = 0{\cdot}65°$ (in alcohol, $c = 0{\cdot}5714$, $l = 0{\cdot}5$); $[\alpha]_D^{?} = 227°$ (Found: C, 80·5; H, 11·2. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). It does not unite additively with bromine, and does not yield esters when treated with acetic anhydride, phthalic anhydride and *p*-nitro-benzoyl chloride, but is dehydrated when warmed with acetic anhydride.

One of us (J. M. R.) is indebted to the Carnegie Trust for a Fellowship which enabled him to take part in this work, and we are grateful to Imperial Chemical Industries Ltd. for a grant which helped to defray the cost.

UNIVERSITY OF GLASGOW. [*Received, May* 11*th*, 1929.]

CLXXIX.—*The Interaction of Bromine with Acetic Anhydride. Part V. Bromination and Chlorination compared* (continued). *Some Properties of Acetic Chloroacetic Anhydride.*

By HERBERT BEN WATSON and CECIL EDWARD GREGORY.

THE results described in Parts II and IV of this series (Orton, Watson, and Hughes, J., 1927, 2458; Watson and Roberts, J., 1928, 2779) indicate that the halogenation of acetic anhydride proceeds by two routes, A and B, as follows:

$$\text{(A)} \qquad CH_3{\cdot}COX + X_2 = CH_2X{\cdot}COX + HX \quad . \quad . \quad (1)$$

$$(CH_3{\cdot}CO)_2O + CH_2X{\cdot}COX \rightleftharpoons CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}COX \quad (2)$$

$$\text{(B)} \qquad (CH_3{\cdot}CO)_2O \rightleftharpoons CH_2{:}C(OH){\cdot}O{\cdot}CO{\cdot}CH_3 \quad . \quad . \quad . \quad (3)$$

$$CH_2{:}C(OH){\cdot}O{\cdot}CO{\cdot}CH_3 + X_2 = CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \quad (4)$$

the ultimate products (acyl halide and monohalogenated acid; Gal, *Ann. Chim. Phys.*, 1862, **66**, 187) then being formed by the further reactions

$$(CH_3{\cdot}CO)_2O + HX \rightleftharpoons CH_3{\cdot}COX + CH_3{\cdot}CO_2H \quad . \quad (5)$$

$$CH_3{\cdot}CO_2H + CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 \rightleftharpoons CH_2X{\cdot}CO_2H + (CH_3{\cdot}CO)_2O \quad (6)$$

Section A of this scheme is supported by the results of Brückner (*Z. angew. Chem.*, 1928, **41**, 226), who has isolated, at certain stages of the chlorination of acetic anhydride, fractions having the boiling points of chloroacetyl chloride and acetic chloroacetic anhydride, respectively. Further, the production of acetyl bromide from acetic anhydride and bromoacetyl bromide (equation 2) has already been demonstrated (Part II), and the authors now find that, on distillation of a mixture of acetic anhydride and chloroacetyl chloride, the products are acetyl chloride and either acetic chloroacetic anhydride (b. p. 80—85°/20 mm. Found: Cl, 25·9. Calc. for $CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3$: Cl, 26%) or chloroacetic anhydride [m. p. 46·5°; compare Bischoff and Walden, *Ber.*, 1894, **27**, 2949. Found: Cl, 41·1. Calc. for $(CH_2Cl{\cdot}CO)_2O$: Cl, 41·5%], depending upon the relative proportions of the reagents.

The halogenation of acetic acid has been shown (Watson, J., 1925, **127**, 2067; 1928, 1137; Part IV of this series) to proceed through the reactions

$$CH_3{\cdot}COX + X_2 = CH_2X{\cdot}COX + HX \quad . \quad . \quad (7)$$

$$CH_2X{\cdot}COX + CH_3{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}COX + CH_2X{\cdot}CO_2H \quad (8)$$

any reaction of the halogen with the enolic form of the acid being negligible. In both chlorination and bromination, the introduction

of a small quantity of acetic anhydride leads to a rapid reaction *after* an initial period of relatively low but increasing speed; there is no such initial period if an acyl halide is introduced, and the velocity is now proportional to the qnantity of acyl halide. These facts leave no doubt that the halogenation proceeds through the halide, and not through the anhydride as suggested by Hentschel (*Ber.*, 1884, **17**, 1286), Shaw (J., 1923, **123**, 2233), and Brückner (*loc. cit.*). The period of increasing velocity clearly represents the time needed for complete conversion of anhydride into acyl halide.

The reaction of acetic acid with one of its halogenated halides (equation 8) has not previously been studied fully, although acetyl bromide has been isolated by one of us (Watson, J., 1928, 1138) by distilling the acid with bromoacetyl bromide. The results described below indicate that reaction 8 occurs in two stages, the mixed anhydride of acetic and halogenated acetic acids being an intermediate product, thus :

$$CH_2X{\cdot}COX + CH_3{\cdot}CO_2H \rightleftharpoons CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \quad (9)$$

$$CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \rightleftharpoons CH_2X{\cdot}CO_2H + CH_3{\cdot}COX \quad (10)$$

Acetic chloroacetic anhydride was prepared by the method of Anthoine (*Jahresber.*, 1883, 1032), *viz.*, by dropping chloroacetyl chloride into a paste of anhydrous sodium acetate (slight excess) and ether. The reaction mixture was kept cool during the addition, and then refluxed at 100°, and the mixed anhydride was obtained from the ethereal solution as a colourless oil. On heating it decomposed, yielding molecular quantities of acetic anhydride and chloroacetic anhydride (Found : Cl, 41·4%) :

$$2CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 = (CH_3{\cdot}CO)_2O + (CH_2Cl{\cdot}CO)_2O \quad (11)$$

An analogous decomposition of the corresponding brominated anhydride is reported by Gal (*Z. Chem.*, 1870, 597). When acetic chloroacetic anhydride is refluxed with a molecular proportion of chloroacetic acid, acetic acid and chloroacetic anhydride (Found : Cl, 41·2%) are formed :

$$CH_2Cl{\cdot}CO_2H + CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 = CH_3{\cdot}CO_2H + (CH_2Cl{\cdot}CO)_2O \quad (12)$$

Reaction of the mixed anhydride with hydrogen chloride takes place readily at room temperature, the products being acetyl chloride and monochloroacetic acid (Found : Cl, 37·5. Calc. : Cl, 37·6%), as represented in equation 10.

A knowledge of these properties of acetic chloroacetic anhydride renders it easy to understand the reactions which occur when acetic acid and chloroacetyl chloride are heated together. On refluxing molecular quantities of these reagents (120 g. and 225 g.

respectively) at 100°, a considerable amount of hydrogen chloride was evolved (giving a loss in weight of 60 g.), and the following were obtained by fractionation at atmospheric pressure: (*a*) 50 g. of acetyl chloride, distilling at 54°, (*b*) 30 g. at 54—150°, giving on refractionation some acetyl chloride and acetic anhydride but principally acetic acid, (*c*) 70 g. at 150—200°, yielding on redistillation a considerable quantity of acetic acid, and a white solid, m. p. 38—47°, containing 39·6% Cl and consisting of a mixture of chloroacetic acid and its anhydride, (*d*) 135 g. of chloroacetic anhydride (m. p. 45·2°. Found: Cl, 41·3%). The production of large quantities of acetyl chloride, acetic acid, and chloroacetic anhydride, with relatively small amounts of chloroacetic acid and acetic anhydride, may be attributed to the initial formation of acetic chloroacetic anhydride (equation 9), followed by reaction of the mixed anhydride with hydrogen chloride (equation 10) and with chloroacetic acid (equation 12), and to some extent by decomposition into acetic and chloroacetic anhydrides (equation 11). When, after removal of acetyl chloride, the remaining mixture was distilled under reduced pressure, a fraction boiling at 80—85°/20 mm. consisted mainly of acetic chloroacetic anhydride (Found: Cl, 24·9%). It is clear, therefore, that the reaction of chloroacetyl chloride and acetic acid leads, in the first instance, to the formation of acetic chloroacetic anhydride, which may then undergo various other changes according to the experimental conditions. In the chlorination of acetic acid at 100°, the hydrogen chloride present in the system (from reactions 7 and 9) will bring about the conversion of the mixed anhydride into chloroacetic acid and acetyl chloride (equation 10), for this reaction proceeds readily even at room temperature.

The scheme previously put forward to represent the halogenation of acetic acid is thus completely confirmed, with the single modification that reaction (8) may be written in the two stages indicated, for the experimental results lead inevitably to the conclusion that the halogen reacts with the acyl halide, the monohalogenated acid being formed as the result of a reaction between the acid and the substituted halide. This is the only mechanism which is in complete harmony with the results of experiment.

The authors wish to express their thanks to Professor Orton, F.R.S., for his interest in the work, to the Chemical Society for a grant from the Research Fund, and to Imperial Chemical Industries Ltd. for a grant made to this Department.

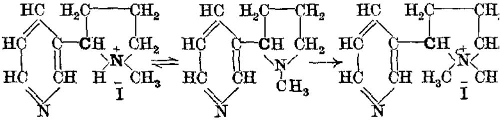
UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR. [*Received, May 17th*, 1929.]

CLXXX.—*The Properties of Nicotine and its Derivatives. Part I. Molecular Extinction Coefficients.*

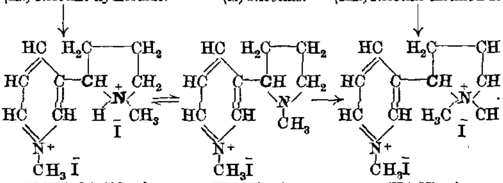
By Thomas Martin Lowry and William Vivian Lloyd.

The optical properties of nicotine are of interest on account of the simple structure of the compound and its exceptional optical activity. Measurements of the optical rotatory power of the base for 27 wave-lengths from 6708 to 4046 Å.U. (Lowry and Singh, *Compt. rend.*, 1925, **181**, 909) have shown that its rotatory dispersion is approximately simple, the reciprocal $1/\alpha$ tending towards a zero value at $\lambda^2 = 0{\cdot}06$, $\lambda = 2450$ Å.U. The refractive indices have also been measured for 13 wave-lengths from 7685 to 4341 (Gifford and Lowry, *Proc. Roy. Soc.*, 1927, *A*, **114**, 592) but without any attempt to correlate the data either with the rotatory dispersion or with the absorption spectrum of the base.

1. *Asymmetric Carbon and Nitrogen.*—The principal compounds investigated during the present research are formulated below :



(II.) Nicotine hydriodide. (I.) Nicotine. (III.) Nicotine methiodide



(V.) Hydriodide of *iso*methiodide. (IV.) Nicotine *iso*methiodide. (VI.) Nicotine dimethiodide.

(i) The base (I) contains a single asymmetric carbon atom, which forms part of a saturated pyrrolidine ring; but it is also linked directly to the aromatic ring of the associated pyridyl radical and it is to this unsaturated system that we must look for an explanation of its selective absorption in the ultra-violet region and of the main characteristics of its rotatory dispersion. According to the usual conventions, nicotine does not possess an asymmetric nitrogen atom, since the tervalent nitrogen of the pyridyl ring can be

formulated with a double bond, and the tervalent nitrogen of the pyrrolidine ring is generally regarded as having a planar configuration. This conclusion is based on the failure of attempts to resolve unsymmetrical amines of the type $NR_1R_2R_3$, but the alternative view, that the non-resolution of these compounds may be due to the small stability of an incomplete tetrahedron rather than to the existence of a stable planar symmetry, is not excluded, and in the case of nicotine would be expected to give rise to unequal concentrations of the *d*- and *l*-nitrogen atoms under the influence of the fixed asymmetry of the adjacent carbon atom of the base.

(ii) The salts (II), on the other hand, contain a quaternary nitrogen atom which is obviously asymmetric and is perhaps a unique example of the occurrence of an asymmetric atom other than carbon in a natural organic compound (Lowry, *Nature*, 1926, **117**, 417). In view, however, of the conditions under which salt *formation takes place, it is clear that the proportion of d- and l-nitrogen atoms will be controlled in the first instance by the fixed* asymmetry of the molecule; and the ready dissociation of the salts of tertiary amines makes it unlikely that these *d*- and *l*-components could be separated permanently. Even, therefore, if we suppose that the crystalline hydrochloride is really a pure *l*-C, *d*-N salt, it is probable that this would pass on dissolution into an equilibrium mixture of the *ld*- and *ll*-forms, and that this process would be too rapid even to give rise to mutarotation under normal conditions of observation.

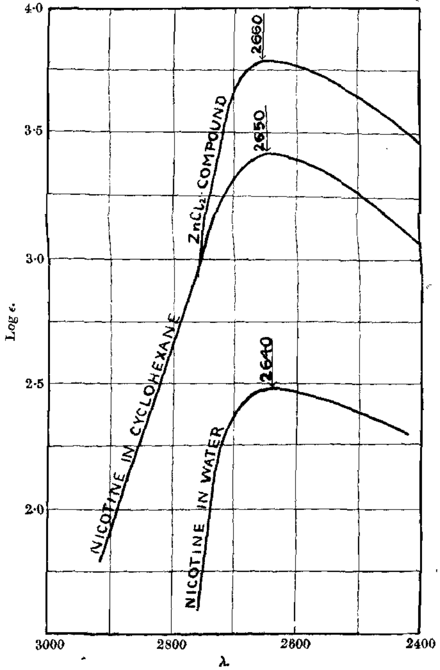
(iii) In the methiodides (III and VI) the pyrrolidine nitrogen is again quaternary, but is not asymmetric, since it is now linked to *two* methyl groups; the *iso*methiodide (IV), on the other hand, is in the same condition as nicotine, since the base contains a planar (?) atom of tervalent nitrogen which becomes quadricovalent and asymmetric in its salts (V).

2. *Molecular Extinction Coefficients.*—The absorption spectrum of nicotine has been examined by Dobbie and Fox (J., 1913, **103**, 1193), who observed a single absorption band at $1/\lambda = 3840$ ($\lambda = 2600$ Å.U.) " almost midway between the heads of the bands for α- and β-picoline " (Baly and Baker, J., 1907, **91**, 1122; Purvis, J., 1909, **95**, 296). The head of the band was at 56 mm. of *N*/5000-solution, so that $\log \epsilon = 3$, approximately, presumably in alcoholic solution. In the present experiments, the molecular extinction coefficients of the base were measured both in water and in *cyclo*hexane, and a number of soluble salts, including three methiodides, were also examined in water. The results of the observations are plotted in Figs. 1 and 2, and the positions of the maxima are set out in Table I.

The constancy, at about 2650 Å.U., of the wave-length of maximum absorption is very striking, in view of the two-fold change of structure (namely, the conversion of a tervalent into a quinque-

FIG. 1.

Absorption spectra of nicotine and its zinc chloride compound.



valent atom of nitrogen and of a neutral molecule into a kation) which accompanies the formation of the methiodides and of the salts. It can be explained, however, if we remember that in many

of its properties the ion $\overset{+}{N}H_4$ resembles the molecule CH_4 even *more closely than does the molecule* NH_3. The aromatic character of the pyridyl ring is therefore preserved intact in these derivatives,

FIG. 2.

Absorption spectra of methiodides.

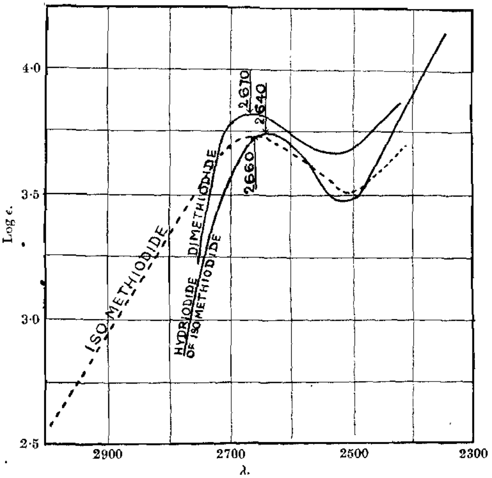


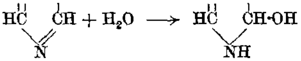
TABLE I.

Maxima in Absorption Spectra.

	Substance.	Solvent.	Log ε.	λ.
I'	*Nicotine*	*Water*	2·49	2640
I	Nicotine	*cyclo*Hexane	3·43	2650
	Zinc chloride compound	Water	3·79	2660
IV	*iso*Methiodide	Water	3·74	2660
V	*iso*Methiodide hydriodide	Water	3·75	2640
VI	Dimethiodide	Water	3·83	2670

in spite of its ionic character. There is, indeed, no important contrast between the four "quaternary" compounds, for which log ε = 3·8 at 2660 Å.U. and the free base in *cyclo*hexane, where log ε = 3·4 at 2650. On the other hand, when the base is dissolved

in water, the maximum falls to log $\varepsilon = 2{\cdot}5$ at 2640, and is nearly ten times *less* intense than in *cyclo*hexane. This cannot be due to any mere failure of the base to combine with the water, since this would make the absorption in water similar to that in *cyclo*hexane; and still less can it be explained by the formation of an ionised ammonium hydroxide, $C_{10}H_{14}N_2 + H_2O \longrightarrow [C_{10}H_{15}N_2]^+OH^-$, since the quaternary ion is three times *more* absorbent than the free base instead of ten times *less*. We are, therefore, obliged to fall back once more on the theory of Moore and Winmill (J., 1912, **101**, 1635) that aqueous solutions of weak bases contain un-ionised hydrates, and to suppose that in the case of nicotine this compound has an absorption which is at least ten times smaller than that of the free base, or may indeed not absorb at all but liberate 10% of the free base by dissociation. In view of the experiments of Decker and Kaufmann (*J. pr. Chem.*, 1911, **84**, 425) on the methyl*iso*quinolinium bases, it may be suggested that the hydrate is formed by the saturation of a double bond of the aromatic ring, giving rise to a pseudo-base from which the picoline-like structure has disappeared, leaving only two conjugated double bonds, in much the same condition as in butadiene.*



In this way we can understand why water behaves differently from inert solvents, and also from acidic hydrides which contain a more ionisable radical than hydroxyl, and which are therefore less ready to form non-ionised pseudo-salts. Since the equilibrium is evidently thrown right over to the side of the pseudo-base, the great readiness with which nicotine is oxidised is in agreement with the observation of Decker and Kaufmann that, although the "ammonium" base from *iso*quinoline methiodide is very stable, its aqueous solutions showing no change even on exposure to air for 72 hours, the isomeric "carbinol" base undergoes atmospheric oxidation very readily.

In conclusion, attention may be directed to the development by the three methiodides (IV), (V), (VI), in the region beyond the absorption band, of a strong "general absorption," which is not shown by nicotine or its salts; this is perhaps associated with the methylation of the pyridyl nitrogen; but, since no observations were made with the liquid methiodide (of which the purity could not be guaranteed), this conclusion is only a provisional method

* The process of hydration might, of course, also proceed further than this (compare Jephcott, J., 1919, **115**, 104).

f summarising the data now available. Conversely, whilst the nolecular extinction coefficient usually falls very steeply from the naximum on the side of longer wave-lengths, there is a wide extension of absorption towards the visible region in the cases of nicotine n *cyclo*hexane and of the *iso*methiodide in water; the common eature here is the presence of a tervalent nitrogen atom in the pyrrolidine ring. Finally, the four compounds in which the pyridyl nitrogen is ionised, whether with the help of a proton or of a methyl group, all exhibit in aqueous solutions a selective absorption which is twice as great as that of the free base in *cyclo*hexane.

EXPERIMENTAL.

Purification of Nicotine.—The nicotine was decolorised by distillation under 2 mm. pressure in an atmosphere of nitrogen. The zinc chloride salt was then prepared by mixing the colourless nicotine (100 g. in 180 c.c. of 95% alcohol) with concentrated hydrochloric acid (140 g.) and alcoholic zinc chloride (180 c.c. of a solution containing 50 g. in 100 c.c.). The resulting double salt, $C_{10}H_{14}N_2,2HCl,ZnCl_2,H_2O$, was recrystallised three or four times from an equal weight of boiling 60% alcohol, and decomposed by adding potassium hydroxide (160 g. in 190 g. of water) to the salt (100 g. in 190 g. of water). The nicotine was separated, shaken for 24 hours with solid potassium hydroxide, and distilled in a vacuum. The second fraction was stored in a bottle from which air had been removed, but was redistilled before use.

The monohydriodide of the base could not be made to crystallise, but the dihydriodide separated from alcohol in pale yellow crystals, m. p. 195°.

The monomethiodide, prepared by mixing the base with an equimolecular quantity of methyl iodide in methyl alcohol, was a yellow syrup which could not be made to crystallise. It was purified by precipitation from chloroform by addition of ether.

The *iso*methiodide was prepared by the action of methyl iodide on the monohydriodide, the hydrogen iodide which had been used to "block" the pyrrolidine nitrogen being finally removed by the action of sodium carbonate. It was recrystallised from methyl alcohol and melted at 164°; its hydriodide crystallised from alcohol as a yellow salt, m. p. 209°. Pictet established its structure by oxidation to trigonelline (*Ber.*, 1897, **30**, 2117).

The dimethiodide, prepared by the action on the base of an excess of methyl iodide in methyl alcohol, was recrystallised repeatedly from methyl alcohol and obtained as a pale yellow compound, m. p. 216°.

*cyclo*Hexane was shaken mechanically with oleum for 2 days,

washed with water, shaken with calcium chloride and lime, distilled from calcium chloride and lime, and frozen eight times. It melted at 6·05°.

The water was of conductivity standard.

Acetic acid (glacial) was distilled from chromic anhydride, frozen and drained several times, and finally distilled from an all-glass apparatus with a long fractionating column. The freezing point of the pure acid was 16·71°.

Acetone was purified through the sodium iodide compound by the Shipsey–Werner method, and was distilled over phosphoric oxide.

The absorption spectra were measured with the new symmetrical form of Bellingham and Stanley's spectro-photometer, usually at a concentration of $M/10,000$.

Summary.

Nicotine and its derivatives show a strong absorption band at 2650 Å.U., which is twice as strong in the zinc chloride compound and in the methiodides, but is ten times weaker when the base is dissolved in water. *It is therefore suggested that the aqueous* solution may contain an un-ionised hydrate or pseudo-base of the type investigated by Decker in the *iso*quinoline series.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, May* 11*th*, 1929.]

NOTES.

Potassium Hexathionate. By JAMES RIDDICK PARTINGTON and ALBERT FRED TIPLER.

THE preparation of potassium hexathionate as described by Weitz and Achterberg (*Ber.*, 1928, **61**, 5399) has been repeated. Analysis of a specimen, very well washed and dried for several days in a vacuum desiccator, gave K, 21·5, 21·8; S, 50·3, 50·6 (Calc.: K, 21·3; S, 52·5%). The sulphur was determined by oxidation with bromine water and precipitation as barium sulphate. The percentage of potassium was found as described by Weitz and Achterberg, by igniting the dry substance and weighing the residue as potassium sulphate, the assumption being made that neither potassium chloride nor other such impurity was present.

Further analyses were carried out by the following method, which, with careful adjustment of details and of apparatus, gave easily reproducible results. (*i*) 10 C.c. of a solution of potassium

chlorate (approx. 0·6N), 30 c.c. of water, and 45 c.c. of concentrated hydrochloric acid were boiled for 1 hour, the evolved gases were absorbed in a solution of potassium iodide (3·5 g. in 35 c.c. of water), and the liberated iodine was titrated with 0·098N-thiosulphate: the normality of the potassium chlorate solution was found to be 0·64. (ii) This procedure was repeated with the addition of 20 c.c. of a solution of the substance (0·2406 g. of a less highly purified specimen in 100 c.c.), but only 10 c.c. of water being used. The volumes of 0·098N-thiosulphate used were 65 c.c. in (i) and 34·5 c.c. in (ii) (mean values).

As the percentage of sulphur in this specimen was 47·2, the ratio of the number of oxygen atoms added to the number of sulphur atoms in the molecule of the oxidised substance is 2·121, which agrees sufficiently well with the ratio 2·167 for hexathionic acid (the ratios for two other possible polythionic acids are heptathionic acid, 2·286; pentathionic acid, 2·000).

Potassium hexathionate was obtained only when the potassium thiosulphate used had been prepared by Foerster and Mommsen's method (*Ber.*, 1924, **57**, 258), represented by the equation $2KSH + 4KHSO_3 = 3K_2S_2O_3 + 3H_2O$. The thiosulphate was obtained as the hydrate $K_2S_2O_3,1\frac{2}{3}H_2O$ (Found: $K_2S_2O_3$, 86·2. Calc.: $K_2S_2O_3$, 86·4%). Several commercial specimens of thiosulphate yielded hardly any hexathionate. A thin film of sulphur produced on the walls of the preparation flask appeared to be prejudicial to the formation of hexathionate. These experiments seem to confirm in their main details the observations of Weitz and Achterberg.—East London College, University of London. [*Received, April 29th*, 1929.]

The Photobromination of Coumarin. By David Matthew Williams.

Berthoud and Nicolet (*J. Chim. Phys.*, 1928, **25**, 40) have shown that the photobromination of α-phenylcinnamonitrile in carbon tetrachloride leads to an equilibrium. α-Phenylcinnamonitrile resembles coumarin, in that both will not react with bromine in the dark in a non-hydroxylic solvent (*J.*, 1928, 343). It has now been found that the photobromination of coumarin leads to an equilibrium. In the case of the nitrile it is possible to reach the equilibrium from both ends, since the dibromide is stable for that purpose, but the dibromide of coumarin is too unstable to allow velocity measurements of its decomposition.

The reaction was studied in light from a mercury-vapour quartz lamp and the reacting solutions were placed in tubes of quartz glass on a rotating table at an average distance of 18 inches from the lamp.

When the concentrations of the coumarin and bromine were $1/60M$ carbon tetrachloride being used as solvent, equilibrium was reached in 25 minutes and 85·6% of the bromine had reacted. With chloroform as solvent, equilibrium was reached in 45 minutes and 65·8% of the bromine had reacted. With the nitrile under identical conditions, equilibrium was reached in about 60 minutes in carbon tetrachloride at 40·2% addition and in about 150 minutes in chloroform at 35·4% addition.

In the thermal reaction (*loc. cit.*) the velocity of bromination was invariably greater in chloroform. It seems that the reverse is true for the photobromination.—THE EDWARD DAVIES CHEMICAL LABORATORIES, ABERYSTWYTH. [*Received, May 9th*, 1929.]

A Micro-method for determining Semicarbazones and its Application to the Analysis of Ketones. By RALPH PERCIVAL HOBSON.

HYDROLYSIS with hydrochloric acid decomposes semicarbazide into ammonia and hydrazine. Rimini (*Atti R. Accad. Lincei*, 1903, 12 II, 376) determined semicarbazones by oxidising the hydrazine with an alkaline solution of mercuric chloride and measuring the nitrogen evolved. Maselli (*Gazzetta*, 1905, **35**, i, 267) analysed the pure base and its salts by estimation of the ammonia formed.

Maselli's method was adapted to a micro-scale for semicarbazones with the modification that the mercuric chloride was added to the acid so as to oxidise the hydrazine as it was formed during the hydrolysis. The essential reactions are :

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O = NH_3 + CO_2 + NH_2{\cdot}NH_2.$$
$$NH_2{\cdot}NH_2 + 2HgCl_2 = N_2 + 2Hg + 4HCl.$$

A solution containing 15% hydrochloric acid and 5% mercuric chloride was used and hydrolysis was carried out by boiling under reflux for several hours in a hard-glass test-tube. The ammonia was then determined by Pregl's modified micro-Kjeldahl method ("Quantitative Organic Microanalysis," 1924, p. 99. Transl. by Fyleman); the solution used for making the mixture alkaline was prepared by diluting a 40% solution of sodium hydroxide with an equal volume of a saturated solution of sodium thiosulphate (which is necessary for the decomposition of the mercury ammonium complex).

Experiments were carried out with semicarbazide hydrochloride and the semicarbazones of acetone and *d*-camphor. The results (Table I) show that the reaction is complete in 6 hours for semicarbazide, one of the three nitrogen atoms appearing as ammonia.

TABLE I.

The ammonification of semicarbazide and semicarbazones by *hydrolysis with a solution of hydrochloric acid containing* mercuric chloride (a = ammonia nitrogen expressed as percentage of total nitrogen).

Substance.	Mg.	Hydrolysis (hrs.).	a.	Substance.	Mg.	Hydrolysis (hrs.).	a.
Semicarbazide	9·8	1½	28·3	Acetonesemi-	191·4	7	33·2
hydrochloride	9·4	4	32·8	carbazone	182·2	,,	33·15
	22·3	,,	32·7	*d*-Camphor-	21·0	,,	32·1
	9·4	6	33·2	semicarbazone	24·2	,,	32·6
	22·1	,,	32·7	Semicarbazide	19·3*	8	34·1
	20·5	8	33·5	hydrochloride	14·8†	,,	36·7
Acetonesemi-	64·4	7	33·4	Acetonesemi-	180·5‡	7	34·1
carbazone	30·4	,,	33·3	carbazone			

* 0·1 G. of sucrose added. † 0·1 G. of sucrose added and mercuric chloride omitted. ‡ Mercuric chloride omitted.

The semicarbazones after 7 to 8 hours' hydrolysis react in the same way, yielding one-third of their total nitrogen as ammonia. It is important when dealing with semicarbazones to destroy the hydrazine, as the ketone released or organic impurities, if present, may cause a partial reduction to ammonia; this has been shown to occur when the mercuric chloride is omitted in the hydrolysis of semicarbazones and of a mixture of semicarbazide and sucrose.

This method affords a means for the micro-determination of ketones, provided they can be converted quantitatively into their semicarbazones when present only in small amounts, and has been applied in this way for the analysis of pyrethrum (Tattersfield, Hobson, and Gimingham, *J. Agric. Sci.*, 1929, **19**, 266). It is not necessary to obtain the semicarbazones pure, but the excess of semicarbazide (and, if present, any impurities yielding ammonia on acid hydrolysis) must be removed. The separation of the semicarbazone from the remaining semicarbazide may be carried out (*a*) by precipitation of the semicarbazone with water, (*b*) by evaporating the mixture to dryness and removing the semicarbazide by washing with water, (*c*) by evaporating the mixture to dryness and extracting the residue with ether, the ethereal solution being shaken with water to remove the semicarbazide.—ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN. [*Received, May 8th, 1929.*]

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